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Article

Double-Stranded Metal–Organic Networks for One-Dimensional Mixed Valence Coordination Polymers

Daniel Robertson,[†] John F. Cannon,[‡] and Nikolay Gerasimchuk*,[†]

Department of Chemistry, Southwest Missouri State University, Temple Hall 456, Springfield, Missouri 65804, and Department of Chemistry and Biochemistry, Brigham Young University, Benson Science Building 100, Provo, Utah 84602

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The design of new types of metal–organic networks and the search for unusual crystal architecture represents an important task for modern inorganic and materials chemistry research. A group of new monosubstituted phenylcyanoximes, containing F, Cl, and Br atoms at the 2, 3, or 4 positions, were synthesized using the high yield nitrosation reaction with CH_3–ONO and were spectroscopically (^{1}H NMR, ^{13}C NMR, UV–visible, IR, mass spectrometry) and structurally characterized. Results of X-ray analysis revealed nonplanar trans–anti geometry for 2-chlorophenyl(oximino)acetonitrile, H(2Cl–PhCO); a nonplanar anti configuration for 4-chlorophenyl(oximino)-acetonitrile, H(4Cl–PhCO); and planar cis–syn geometry for 3-fluorophenyl(oximino)acetonitrile, H(3F–PhCO). All arylcyanoximes undergo deprotonation in solutions with the formation of colored anions exhibiting pronounced *negative* solvatochromism in a series of polar protic and aprotic solvents. Nine thallium(I) cyanoximates were obtained using the reaction between hot (~95 °C) aqueous solutions of Tl_2CO_3 and solid powdery monohalogenated arylcyanoximes HL. Crystal structures of two Tl(I) cyanoximates [Tl(2Cl–PhCO) and Tl(4Br–PhCO)] contained centrosymmetric dimeric units $(TlL)_2$ that are connected to a coordination polymer by means of an oxygen atom of the oxime group of the neighboring molecule. Cyanoxime anions act as bridging ligands in both structures where the polymeric motif consists of double-stranded Tl–O chains interconnected with the formation of zigzagging Tl_2O_2 planar rhombes. Thallium atoms form infinite linear arrays with close intermetallic separations. The nearest Tl(I)···Tl(I) distances are 3.838 and 4.058 Å in the Tl(2Cl–PhCO) and Tl(4Br–PhCO) structures, respectively, close to that in metallic thallium (3.456 Å). Monosubstituted phenyl groups are well aligned in π-stacking columns that are perpendicular to the array of Tl(I) atoms and stabilize formed structures. Coordination polyhedrons of thallium(I) in these complexes represent distorted trigonal pyramids with stereoactive lone pair.

Introduction

Delocalized mixed-valence compounds[1,2] have great potential as electric conductors. The discovery of highly conductive nonmetallic substances and reliable superconducting material promises great reduction in future energy and materials consumption for transportation and the use of electricity. So far, ceramics, containing various transition-metal oxides, were found to be high-temperature superconductors above the boiling point of nitrogen.[3] These compounds, however, encounter serious problems such as the instability of crystal lattices associated with the loss of superconductivity over time and after a reiterated strong

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* Author to whom correspondence should be addressed. Phone: (417) 836-5165. Fax: (417) 833-5829. E-mail: nig434f@smsu.edu.

[†] Southwest Missouri State University.

[‡] Brigham Young University.

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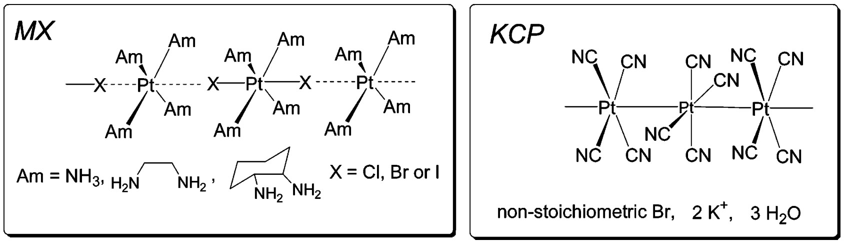
Scheme 1



magnetic field has been applied. Conductive coordination polymers based on an organic ligand network promise certain advantages over ceramics. An electron transfer (hopping) between different oxidation states is a key phenomenon in the electric conductivity of mixed-valence compounds.[4] There are ongoing investigations in classical one-electron-transfer compounds based on copper(I/II),[5] ruthenium(II/III),[6] iron(II/III),[7] manganese(II/III or III/IV),[8] and other (Cr,[9] Co[10]) redox pairs. There also is a growing interest in the two-electron-transfer mixed-valence compounds based on gold(I/III),[11] nickel(II/IV),[12] and thallium(I/III)[13] and the continuous awareness of platinum(II/IV) pairs in *MX* and *KCP* systems.[14] Both systems represent classical one-dimensional solids that possess significant electrical conductivity (Scheme 1).

Thallium and platinum received substantial attention in numerous spectroscopic,[15] structural,[16] and theoretical studies.[17] Thallium is especially attractive since it has a two-electron transition (Tl$^+$ ⇔ Tl^{3+}) from the top 6p valence shell; these electrons are thought to be coherent and form a pair similar to that offered by Cooper et al.[18] Established by Zusman et al.,[15a,17c] the values for the rate of the Tl$^+$/Tl^{3+} transition are $\sim 2 \times 10^3$ s^{-1} and $\Delta G \sim 0.76$ eV (∼6130

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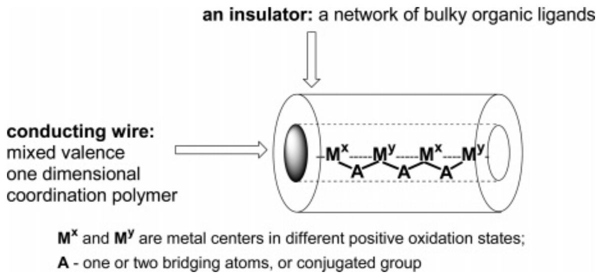
Scheme 2



cm^{-1}), making a formation of mixed-valence thallium-based coordination polymers that exhibit electron hopping achievable. Interesting examples of heterometallic Tl−Pt and polymeric chain Tl−Au compounds were recently reported.[19] A generation of mixed-valence species can be achieved through the cocrystallization of two homovalent coordination compounds[14a,d] or through the controlled partial oxidation of the low-valent metal complexes using halogen vapors or an electric current.[20]

There are three important factors that guide the search for mixed-valence coordination polymers that may exhibit an electrical conductivity and even lead to high-temperature superconductivity. These are (1) the formation of a well-organized one-dimensional polymeric motifs such as columns, chains, or narrow sheets connected by nonbonding interactions; (2) a close spatial location of metal ions in the crystal lattice due to appropriate bridging atoms/groups or direct metal−metal interactions; and (3) similar coordination geometries and bonding properties for metal centers in different oxidation states. The latter property leads to a low energy barrier between two different oxidation states and creates the condition for electron transport (hopping),[4] induced by light or temperature.

One of the key conditions for success in the search for conducting mixed-valence compounds and materials is the discovery and exploration of new bridging ligand systems that can ensure formation of the one-dimensional polymeric structures of complexes (Scheme 2).

Our attention turned to oximes, a versatile group of stable organic molecules. The oximes form numerous coordination compounds[21] with a majority of metal ions including those existing in two or more different oxidation states. Cyanoximes,[22] in particular, represent a new and interesting class of excellent ligands with the general formula NC−C(═N−OH)−R, where R is an electron-withdrawing group such as CN,[23] amide,[24] thioamide,[25] keto,[26] carboxylic esters,[27] hydrazide,[28] or 2-heteroaryl.[29] Since cyanoximes show an unprecedented variety of different binding modes to metal ions,[30] these molecules are far better ligands than conventional monoximes and dioximes. Also, the cyanoximes possess higher acidity than the latter and, therefore, more easily undergo deprotonation to form anionic species that readily interact as nucleophiles (bases) with metal cations. Thus, the cyanoximes' pK_a values[22a] range from 4.5 to 7.5 and are 2−4 orders of magnitude lower than those for acetone-oxime (10.8), acetophenone-oxime (9.2), and dimethylglyoxime (10.2).[49,61] There are about three dozen cyanoximes known and studied up to date. The vast majority

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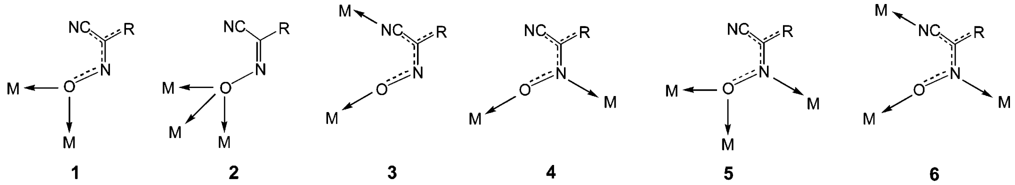
Scheme 3



of these ligands act as chelators in metal complexes, but the bridging function of the ligands is known as well. Cyanoximate anions, as superior ampolydentate organic ligands,[31,32][42] are a good choice for the design of metal−organic networks that *support* one-dimensional polymeric motifs in the structures. Thus, cyanoximes exhibit an extensive bridging function via donor atoms of the NC−C(NO)− fragment in numerous complexes (Scheme 3). Often, bridging is accompanied by the formation of five-membered chelate rings as a result of the participation of donor atoms (O, N, or S) present on different R group.[25,30,45]

Anionic bridging ligands may facilitate an electric conductivity in formed mixed-valence coordination polymers with closely located metal centers (Scheme 2). Presented in Scheme 4, monosubstituted halogenated arylcyanoximes and their metal complexes were largely unknown prior to this investigation. These molecules, however, represent an interesting set of organic flexible ligands that cannot form chelate metallocycles and may not only act as bridging groups to form coordination polymers but also feature π-stacking interactions. Therefore, we selected nine arylcyanoximes, shown in Scheme 4, for our studies.

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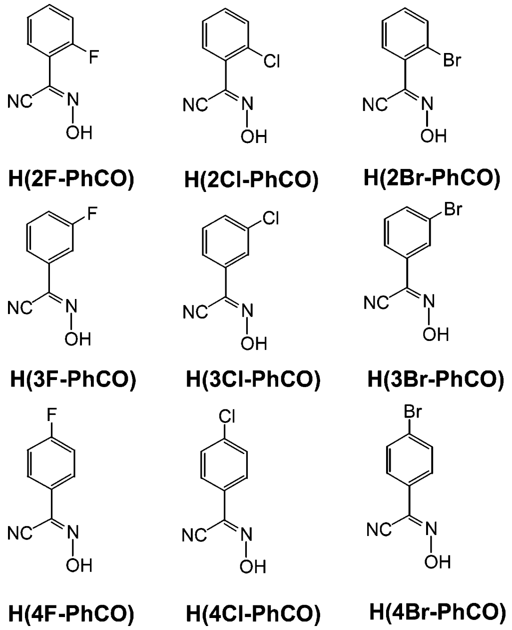
Scheme 4



In general, Tl(I) forms coordination compounds of several structural types: distorted Tl_4O_4 cubes in tetramers or cages;[64,66] planar Tl_2O_2 or nonplanar $[Tl_2X_2]^{2-}$ (X = S, Se, Te) rhombic units in molecular complexes;[63,67] isolated or polymeric Tl−Pt, Tl−Au, or Tl−Cu clusters;[65] and zigzag polymers. A very interesting polymeric staircase structure consisting of Tl_2O_2 skewed rhombes in thallium(I) ortho-nitrophenolate was reported recently.[62] Planar conjugated anionic cyanoximes were found in ionic alkali metal salts[42b,59] and chelate complexes of transition metals.[24a,30a,60] In both of these types of compounds, cyanoximes exist as *nitroso* anions. In some cases, alkali metals such as sodium, potassium,[43] and cesium[42b] often form stable ionic "acid salts" of *monoprotic* cyanoximes of MHL_2 composition (L = amidecyanoximes and 2-heteroaryl-cyanoximes). Contrary to those salts, thallium(I) forms cyanoximates of TlL with 1:1 stoichiometry with a significant degree of covalent bonding between the metal center and ligand. Previously, we discussed the synthesis and crystal structures of several thallium(I) cyanoximates.[45] The results of these studies are summarized in Table 1. There are two different types of Tl cyanoximates, those that contain (a) a nonplanar bridging anion in the *oxime* form and those that contain (b) a planar conjugated anion in the *nitroso* form in cases where the ligands can form chelate complexes. These complexes are reflected in binding modes **2** and **4**−**6**, respectively (Scheme 3). Careful analysis of the known structures of complexes has necessitated a search for new ligands for metal−organic networks, ligands that are able to form stable one-dimensional coordination polymers with spatially close linear arrays of metal ions.

Halogenated arylcyanoximes could provide interesting examples of crystal lattice architecture due to the involvement of halogen atoms in the coordination to the metal center. The affinity of Tl(I) toward halogenides has been well-established and resembles that for Ag(I) cations.[33] The presence of halogen atoms at the 2, 3, or 4 positions on the phenyl group of these cyanoximes may provide additional support for the coordination of ligands to the monovalent thallium centers. *Ortho-assistance*—support upon coordination of the ligands containing halogen atoms (Cl, Br, or I) in aromatic compounds to the metal center—has been established for numerous organometallic complexes of transition metals.[34] The Ln−F dative interactions were recently reported for several lanthanide fluorinated thiolate complexes.[35] A rare extra-coordination of fluorine atoms leading to the formation of a planar five-membered chelate ring in Zn(II) 2,6-difluorophenol complexes was found as well.[36] Also, the weak extra-coordination of halogen atoms from neighboring molecules in the samples of solid Ag(I) and Tl(I) halomethanesulfonates was recently discussed.[37]

Some results of the first part of our investigation dealing with the synthesis and characterization of Tl(I) monosubstituted arylcyanoximates are reported here.

Results and Discussion

1. Ligands Characterization. With the exception of 2-chlorophenyl(oximino)acetonitrile H(2Cl−PhCO),[58] none of the monosubstituted arylcyanoximes shown in Scheme 4 were known prior to this study. These compounds undergo deprotonation with the formation of yellow anions; the color originates from low-intensity $n \rightarrow \pi^*$ transitions ($\epsilon = 20-200\ M^{-1}\ cm^{-1}$) of the nitroso chromophore in the visible region of the spectrum. Anionic cyanoximates possess, in alkali metal salts, conjugated planar structures[22,30−32] in which the negative charge is delocalized throughout the anion, and they may be described using several resonance forms, as shown in Scheme 5. This behavior is consistent with that observed earlier for other cyanoxime ligands[22] where the majority of resonance structures of cyanoxime anions represent nitroso forms. Indeed, in ionic alkali metal or ammonium salts, there are nitroso anions, judging from the shorter N−O distances versus the C−N bond length in the fragment.

Figure 1 shows typical spectral changes, such as the bands' batochromic shift, indicating charge delocalization during the deprotonation of cyanoximes. Traditionally, the solvent effect on absorption in the UV and visible regions of spectra has been used for the characterization of new chromophores and

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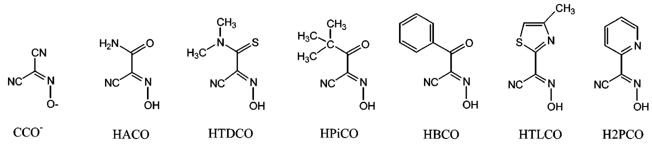
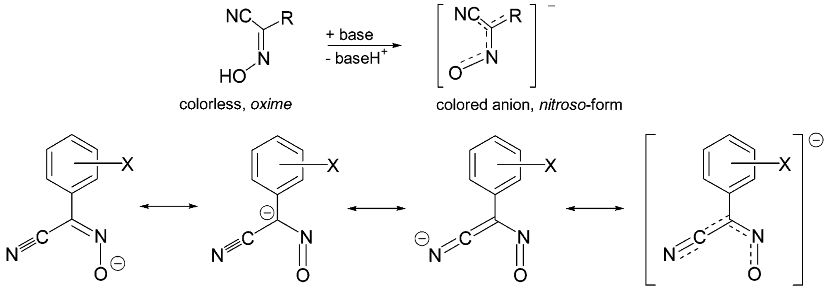
Table 1. Results of the Structural Investigation of Some Tl(I) Cyanoximates

complex[a]	Tl···Tl distance, Å	metal center coordination number	structure, motif, comments	ref
Tl(ACO)	4.47	5	ruffled, regular Tl_2O_2 rhombes	45c
Tl(BCO)	4.41	3	isolated Tl_2O_2 rhombes	45d
Tl(CCO)	4.26	7	very complicated 3D network	56
Tl(2PCO)	4.13	4	well-organized Tl···O chains	33a
Tl(4Br−PhCO)	4.06	3	well-organized, irregular Tl_2O_2 sheet	this work
Tl(TDCO)	4.05	7	well-organized Tl···S and Tl···O chains	45b
Tl(PiCO)	4.03, 4.06	4,5	isolated, very complex TlL trimers	45i
Tl(2Cl−PhCO)	3.84	3	well-organized irregular Tl_2O_2 sheets	this work
Tl(TLCO)	3.65	4	isolated dimers TlL; NO group disordered	45k
Tl metal	3.45	8	face-centerd cubic lattice	54

[a] 1:1 stoichiometry compounds with abbreviated ligand structures, which are shown below:



Scheme 5



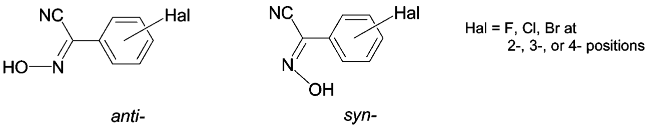
better understanding their electronic structures. It is interesting to note that deprotonated monosubstituted arylcyanoximes (cyanoximate anions) exhibit a pronounced negative solvatochromic effect[38] (Figure 2). There is a substantial difference between the λ_{max} values of the $n \rightarrow \pi^*$ transition in the visible region of the spectra of cyanoximate anions in the protic solvents ROH (R = H, CH_3, C_2H_5, n-C_3H_7, and t-C_4H_9) and those of aprotic solvents such as acetone, CH_3CN, DMF, and DMSO. The energy gap, for example, between absorbances in CH_3OH (at 392 nm) and DMSO (at 443 nm) for solutions of tetrabutylammonium $(4Br{-}PhCO)^-$ is 35.1 kJ/mol, which is consistent with a hydrogen bond of medium strength.

Linear correlations between the positions of bands in the spectra of ionic tetrabutylammonium cyanoximates, $N(C_4H_9)_4{}^+L^-$, and between solvent parameters such as pK_a and Kosower's specific solvation energy[39,40] Z were found for several of the alcohols ROH used (Figure 3). The highest energy for optical transitions in UV−visible spectra of cyanoximate anions was observed for aqueous solutions and is typical of negative solvatochromism.

The solvation by aprotic solvents such as DMF and DMSO significantly lowers the energy of the $n \rightarrow \pi^*$ transition in the visible region of the spectra [Figure 2; Supporting Information, S1 (S1, S2, S3, etc. refer to sections in the PDF Supporting Information file; refer to the key given in the Supporting Information section at the end of this paper for details)].

Hydrogen bonding with solvent molecules is strongest in aqueous solutions, and the energy of this transition in spectra is the highest among other solvents. Again, this is evidence for negative solvatochromism, at which the value of the dipole moment of a molecule or ion in the excited state is smaller than that in a ground state,[38] reflecting a charge transfer from the terminal oxygen atom of the NO group into nitrogen or carbon atoms of the oxime fragment in the excited state.

In some cases, the ^{13}C NMR spectra of the synthesized monosubstituted arylcyanoximes contained only one set of signals, indicating the presence of only one geometrical isomer,[41] syn or anti, in solutions at room temperature. These compounds are H(2F−PhCO), H(2Cl−PhCO), H(2Br−PhCO), H(3Br−PhCO), and H(4F−PhCO). An anti isomer is considered to be more favorable. The ^{13}C NMR spectra of other cyanoximes, such as H(4Br−PhCO), H(4Cl−PhCO), H(3Cl−PhCO), and H(3F−PhCO), contain two sets of signals due to the presence of two isomers in the DMSO-d_6 solutions at room temperature. The ^1H NMR spectra of these mixtures also displayed a double set of lines strongly overlapped in the aromatic region.



The most intense signals in the ^1H NMR spectra of synthesized HL (L = monosubstituted arylcyanoxime; Scheme 4) in DMSO-d_6 solutions were tentatively assigned to the most sterically preferable anti configuration. The ^1H

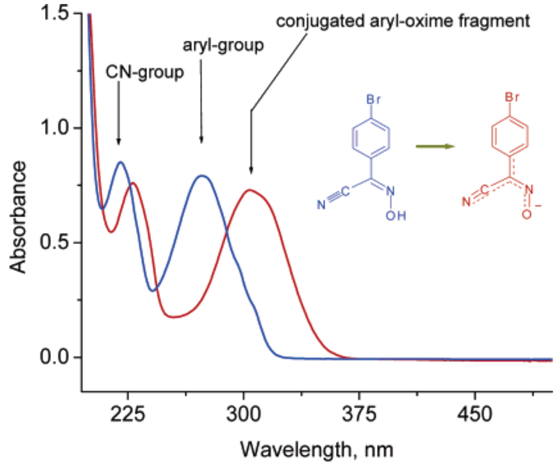


Figure 1. UV spectra of solutions of protonated (blue) and deprotonated cyanoxime (red, as tetrabutylammonium salt) showing a batochromic shift of $\pi \rightarrow \pi^*$ transition bands due to conjugation in an anion. Solution in EtOH at 5×10^{-4} M concentration in a 1 mm quartz cuvette; $T = 296$ K.

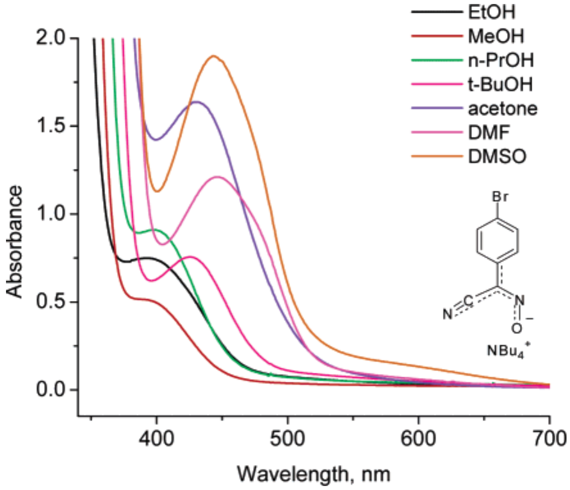


Figure 2. Solvatochromic series for solutions of NBu$_4^+$(4Br−PhCO)$^-$ in different solvents. Isomolar solutions (5 mM) in 1 cm quartz cuvette; $T = 296$ K.

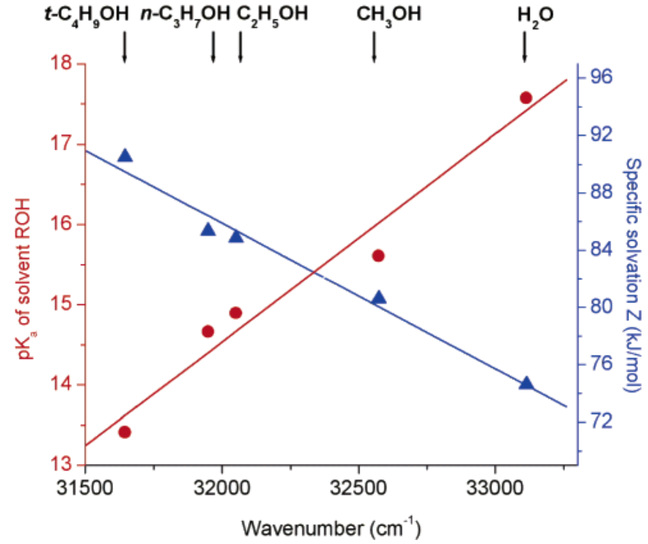


Figure 3. Correlations between absorbance maximum of conjugated aryl-oxime band ($\pi \rightarrow \pi^*$ transition) in UV spectra of NBu$_4^+$(3F−PhCO)$^-$ and solvent ROH parameters such as pK_a (red) and specific solvation energy Z (blue). Red: linear fit for $y = A + Bx$, with $A = -386.8$, $B = 0.0145$; $R = 0.981$. Blue: linear fit for $y = A + Bx$, with $A = 74.10$, $B = -0.001\ 82$; $R = -0.90$.

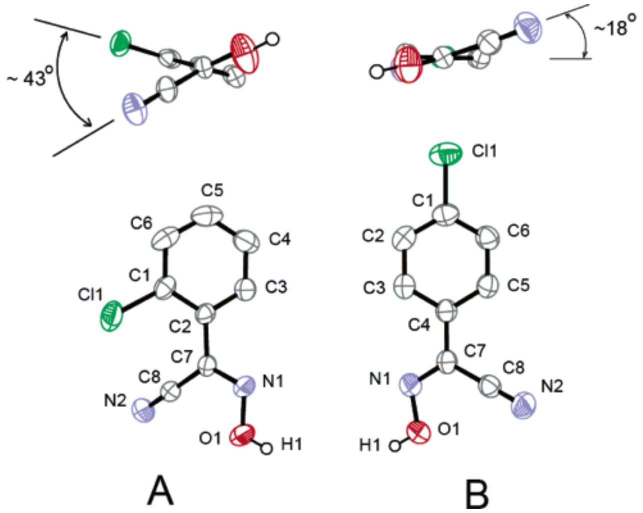


Figure 4. Molecular structure and numbering scheme for nonplanar arylcyanoximes H(2Cl−PhCO) (A) and H(4Cl−PhCO) (B) drawn at the 50% thermal ellipsoids probability level. Hydrogen atoms, with the exception of H1, are omitted for clarity.

NMR spectra of all compounds contained broadened signals of the oxime hydrogen around 14 ppm. Unfortunately, no separate OH signals for syn and anti isomers were found, indicating a fast proton exchange between the two isomers. H(3F−PhCO) in the solid state exists as a mixture of cis−syn and cis−anti isomers with a planar structure. However, according to the X-ray analysis data discussed below, the majority of arylcyanoximes studied up to date adopt only one particular configuration in the solid state.[69] The exact assignment of a particular syn or anti configuration in a solution by the NMR method was beyond the scope of this research because it requires special 2D NOE experiments. Data of room temperature ^{13}C NMR spectroscopy for all synthesized monosubstituted arylcyanoximes are available in the Supporting Information, S2 and S3.

1.1. Crystal Structures of Synthesized Cyanoximes. The halogenated monosubstituted arylcyanoximes represent colorless substances that can be crystallized to form single crystals suitable for X-ray analysis using slow evaporation of solutions in CCl$_4$ or water. All of the crystallized compounds do not contain solvent molecules, contrary to some heterocyclic cyanoximes.[30b,42] Crystallographic data for structures of three protonated arylcyanoximes HL are shown in Table 2.

1.2. Structure of H(2Cl−PhCO). The molecular structure of H(2Cl−PhCO) is shown in Figure 4A. Bond lengths and valence angles in the structure are summarized in Table 3. The cyanoxime is nonplanar and adopts a trans−anti configuration[30b] in the solid state. Thus, the oxime fragment and chlorine atom are on opposite sides of the molecule along the C2−C7 direction. There are two planar fragments in the structure of the molecule: the cyanoxime fragment C8−C7−

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Table 2. Crystallographic Data for Several Synthesized Monosubstituted Arylcyanoximes and Their Tl(I) Complexes

parameter	H(2Cl−PhCO)	H(3F−PhCO)	H(4Cl−PhCO)	Tl(4Br−PhCO)	Tl(2Cl−PhCO)
empirical formula	$C_8H_5ClN_2O$	$C_8H_5FN_2O$	$C_8H_5ClN_2O$	$C_8H_4BrN_2OTl$	$C_8H_4ClN_2OTl$
fw	180.59	164.14	180.59	428.41	383.95
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_{1/c}$	$P2_{1/c}$	$P2_{1/c}$	$P2_{1/n}$	$P2_{1/n}$
a, Å	9.5477(5)	8.8628(18)	11.8836(9)	13.1112(13)	3.8382(7)
b, Å	12.1061(7)	12.533(3)	6.8572(4)	4.0577(4)	11.0065(18)
c, Å	7.6112(5)	7.1450(11)	11.3390(7)	17.0940(17)	20.901(4)
α	90	90	90	90	90
β	111.26(4)	106.577(15)	115.39(5)	92.140(2)	92.447(3)
γ	90	90	90	90	90
vol, $Å^3$	819.9(8)	760.2(2)	834.7(9)	908.8(16)	882.2(3)
Z	4	4	4	4	4
T, K	296(2)	296(2)	293(2)	100(2)	193(2)
λ, A	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
D (calcd), Mg/m^3	1.463	1.433	1.437	3.131	2.891
μ, mm^{-1}	0.412	0.115	0.405	22.124	18.565
F(000)	368	336	368	760	688
reflns collected (independent)	1954 (1436)	1834 (1339)	2003 (1465)	14118 (3213)	5699 (1899)
R (all data)	0.0424	0.0651	0.0411	0.0338	0.0689
wR^2 (all data)	0.0891	0.1301	0.0961	0.0693	0.1650

Table 3. Selected[a] Bond Lengths (Å) and Valence Angles (deg) in the Structures of Three Monosubstituted Arylcyanoximes

H(2Cl−PhCO)				H(4Cl−PhCO)			
bond		angle		bond		angle	
Cl(1)−C(1)	1.374(2)	C(2)−C(1)−Cl(1)	120.75(14)	C(1)−C(6)	1.374(2)	C(6)−C(1)−Cl(1)	119.14(14)
O(1)−N(1)	1.377(19)	C(3)−C(2)−C(1)	117.86(16)	C(1)−C(2)	1.379(3)	C(5)−C(4)−C(3)	118.46(16)
N(1)−C(7)	1.287(2)	C(3)−C(2)−C(7)	118.81(16)	C(1)−Cl(1)	1.738(2)	C(5)−C(4)−C(7)	120.51(15)
N(2)−C(8)	1.134(2)	C(1)−C(2)−C(7)	123.33(18)	C(4)−C(7)	1.467(2)	C(3)−C(4)−C(7)	121.01(15)
C(1)−C(2)	1.398(2)	C(7)−N(1)−O(1)	111.59(14)	C(7)−N(1)	1.289(2)	N(1)−C(7)−C(8)	120.21(15)
C(2)−C(3)	1.392(3)	N(1)−O(1)−H(1)	109.5(14)	C(7)−C(8)	1.449(2)	N(1)−C(7)−C(4)	121.18(14)
C(2)−C(7)	1.477(2)	N(1)−C(7)−C(8)	121.17(15)	C(8)−N(2)	1.134(2)	C(8)−C(7)−C(4)	118.55(13)
C(7)−C(8)	1.448(3)	N(1)−C(7)−C(2)	118.03(15)	N(1)−O(1)	1.378(2)	N(2)−C(8)−C(7)	177.23(18)
		C(8)−C(7)−C(2)	120.71(14)				
		N(2)−C(8)−C(7)	178.5(2)				

H(3F−PhCO)[b]							
bond		angle		bond		angle	
C(2)−F(1)	1.357(7)	F(1)−C(2)−C(3)	116.6(7)	C(7)−N(2b)	1.27(2)	N(1)−C(8)−C(7)	179.0(9)
C(3)−C(4)	1.387(8)	C(5)−C(4)−C(3)	119.3(6)	C(7)−N(2a)	1.334(11)	C(7)−N(2a)−O(1a)	108.3(8)
C(4)−C(5)	1.376(8)	C(5)−C(4)−C(7)	118.7(6)	N(2a)−O(1a)	1.366(13)	C(7)−N(2b)−O(1b)	104.8(11)
C(4)−C(7)	1.467(8)	C(3)−C(4)−C(7)	122.0(6)	N(2b)−O(1b)	1.384(15)		
C(8)−N(1)	1.118(8)	C(8)−C(7)−C(4)	119.4(6)				

[a] The geometry of phenyl group is normal and not shown. [b] Contains a mixture of syn and anti isomers in the same crystal (see Figure 5).

N1−O1 and the 2-chlorophenyl group. The dihedral angle between these planes is ~43°. Distances C7−N1 = 1.287(2) Å and N1−O1 = 1.3769(19) Å and valence angles at C7 in the oxime fragment are normal for cyanoximes.[22,30,31] The shortest distance between the Cl1 and N2 atoms is 3.440 Å. Molecules of H(2Cl−PhCO) are packed into the crystal by means of $\pi-\pi$-stacking interactions and hydrogen bonding between the nitrogen atom N2 of the cyano group (A) and the hydrogen atom attached to the oxygen atom (D) of the oxime group. The parameters for H bonding in the crystal are O1−H1···N2 = 2.904(2) Å, H1···N2 = 2.09 Å, and ∠(DHA) = 173.9°. H-bound molecules of H(2Cl−PhCO) form chains that are connected by "slipped" π-stacking interactions.

1.3. Structure of H(4Cl−PhCO). The molecular structure of H(4Cl−PhCO) is shown in Figure 4B, while valence angles and bond distances for the molecule are presented in Table 3. This cyanoxime also adopts an anti configuration. Since the chlorine atom is at the para position to the cyanoxime fragment, no further cis or trans assignment of geometry can be made. Two planar fragments can be seen in the structure of H(4Cl−PhCO), the aryl group and the cyanoxime group. There are several dihedral angles that describe deviation of the whole molecule from planarity, for example, C3−C4−C7−N1 = 17° and C8−C7−N1−O1 = −1.1°. The distances C7−N1 and N1−O1 are equal to 1.289(2) and 1.3784(18) Å, respectively; these values are normal for cyanoximes.[22,30,31] Hydrogen bonding between H1 of the oxime group and N1(#1) in the cyano group of the neighboring molecule and $\pi-\pi$ stacking interactions are responsible for the packing of H(4Cl−PhCO) molecules into a crystal. This H bond has the following parameters: O1−H1···N2(#1) = 2.8388(19) Å and H1···N2(#1) = 2.03 Å with the angle ∠(DHA) = 171.1°.

1.4. Structure of H(3F−PhCO). The molecular structure of H(3F−PhCO) is shown in Figure 5A. The oxygen and nitrogen atoms of the oxime group in this compound are disordered by two positions, indicating coexistence of the

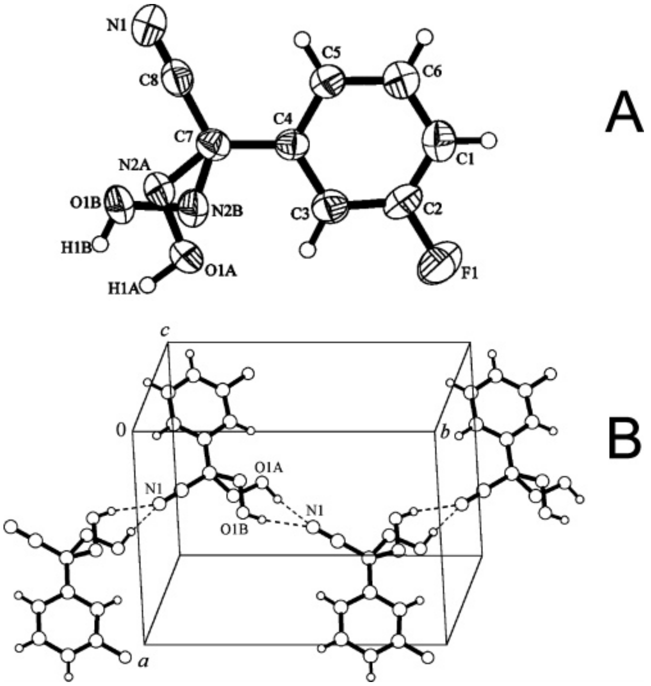


Figure 5. (A) Molecular structure and numbering scheme for planar H(3F−PhCO) that represents a mixture of the syn (60%) and anti (40%) isomers: view of superimposed molecules. (B) H-bonding in the crystal.

two geometrical isomers in the crystal. A detailed analysis of the experimental data set converged to $R = 0.065$ for the structure having 60% of its molecules as syn and 40% of its molecules as anti isomers. The disorder in the CNO fragment in some of the cyanoxime complexes was documented earlier.[31e,45k] Bond lengths and valence angles are presented in Table 3. 3-Fluorophenyl(oximino) acetonitrile, H(3F−PhCO), adopts a planar configuration in the solid-state, being the second documented case of such geometry for protonated cyanoximes after NC−C(NOH)−C(O)NH_2 (ACO).[68] All bond lengths and angles at the oxime carbon atom C7 and nitrogen atoms N2A and N2B are normal for these geometric isomers. The distance H3−O1 = 2.300 Å in the syn isomer can be considered as a long hydrogen bond. The distance F1−H3 is 2.499 Å and is slightly smaller than the distance between fluorine and the closest hydrogen atom H1: F1−H1 = 2.512 Å. This slight tilt toward the H3 atom reflects an attractive interaction between the two atoms. The torsion angles in the skeleton of the molecule around the C4 and C7 atoms are close to 0° (or 180°), reflecting an unexpected planarity of the fluorinated cyanoxime. The values of these angles are C5−C4−C3−C7 = −0.3°, O1−N2−C7−C4 = −179°, and O1−N2−C7−C8 = 179.5°. There is hydrogen bonding in the structure between the H1a atom of the oxime group and the N1 atom of the CN group neighboring molecule, resulting in the formation of a zigzag chain along the *y* direction. Interestingly, the presence of the two isomers does not affect the packing mode of the cyanoxime into a crystal (Figure 5B).

Peculiarities of the stereochemistry for other known cyanoximes are summarized in Table 4.

2. Metal Complexes. The most important IR frequencies for all synthesized protonated arylcyanoximes HL and their Na^+ and Tl^+ derivatives are presented in the Supporting Information, S4. Sodium salts of the ligands were obtained as alternative precursors for monovalent thallium complexes and also for IR-spectroscopic studies of uncoordinated cyanoximates in ionic salts. According to established IR criteria for cyanoxime coordination,[23,45a,i] a low-frequency shift of ν(NO) and ν(CNO) vibrations[45i] compared to those in ionic NaL are evidenced in the bridging binding mode **2** of the oxime fragment (Scheme 3).

2.1. Crystal Growth and Structures of Thallium(I) Cyanoximates. Monovalent thallium easily forms crystals with cyanoxime ligands. However, obtaining quality single crystals of Tl(I) cyanoximates, suitable for X-ray analysis, represents a challenging problem. For example, there is a tendency for Tl^+ organometallic compounds[46] to form fibrous microcrystals of poor quality. There are two major obstacles that affect crystallization of thallium complexes: (a) the fast, within several seconds, formation of very thin fibers or plate-looking crystals upon cooling of hot aqueous solutions of TlL (L = monosubstituted arylcyanoximes) and (b) twinning of the crystals formed. The difference in solubility of TlL in hot and room-temperature aqueous solutions is significant. Therefore, obtaining the second or third crop of crystals from the mother liquors can take weeks. The most successful method of growing suitable quality crystals of TlL is a hot filtration of the reaction mixture into a large mouse test tube, immersed into 4−5 L of water preheated to ∼96 °C in a large Dewar flask equipped with an insulating cap. Cooling of the obtained solution to room temperature takes several days and usually affords X-ray quality crystals of monovalent thallium cyanoximates. Photographs of crystalline samples of some of the obtained thallium(I) cyanoximates are shown in the Supporting Information, S5 and S6. The crystallographic data for the two TlL complexes reported in this work are summarized in Table 2.

2.2. Tl(2Cl−PhCO). The molecular structure of Tl(2Cl−PhCO) represents an interesting centrosymmetric dimer and is shown in Figure 6A, while bond lengths and valence angles in the structure of the complex are summarized in Table 5. The anion in the structure is in the oxime form and adopts a nonplanar trans−anti configuration similar to that in H(2Cl−PhCO). There are two planar fragments in the structure: the 2-chlorophenyl group and the cyanoxime fragment. The value of the torsion angle at the C3−C7 bond in the thallium(I) complex (48.3°) is close to that for the protonated cyanoxime ligand (43°). There are small changes in bond lengths and angles in the oxime fragment in the Tl(I) complex as compared to those in the protonated cyanoxime. It is interesting to compare bond lengths N−O and C−N in the oxime group in the uncoordinated ligand and in its metal complex. Thus, O1−N1 = 1.377 Å and N1−C7 = 1.287 Å for H(2Cl−PhCO), while the same distances are 1.364 Å and 1.310 Å, respectively, in the structure of Tl(2Cl−PhCO) (Tables 3 and 5). The sum of these bond lengths for both compounds is almost identical: 2.664 Å in the ligand itself and 2.674 Å in its thallium(I) complex. This evidences redistribution and decreasing of the electron

Table 4. Stereochemical Peculiarities of Several Cyanoxime Ligands

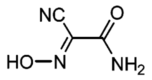
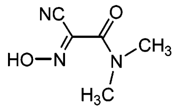
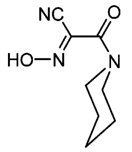
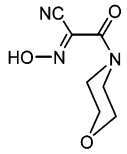
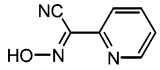
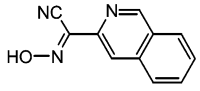
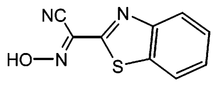
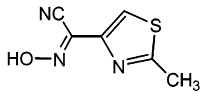
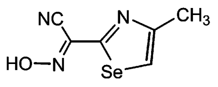
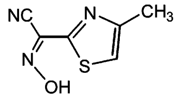
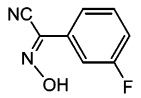
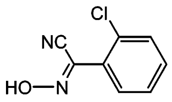
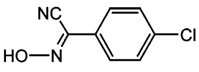
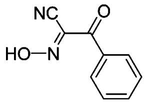
Compound	Structure, Comments	Ref.
 HACO	*Solid state: planar, *trans-anti* geometry. Two independent molecules in the unit cell. **Solutions (dmso-d$_6$): *anti*-isomer only; restricted rotation around C-N amide bond: ΔG =67.7 kJ/mol; $T_{(coalescence)}$= 323 K	57 30c
 HDCO	Solid state: non-planar, *trans-anti* geometry. Dihedral angle between planar oxime- and amide- O-C-N groups is 28° Solutions (dmso-d$_6$): *anti*-isomer only; restricted rotation around C-N amide bond: ΔG = 72.6 kJ/mol; $T_{(coalescence)}$=353 K	4c 30c
 HPiPCO	Solid state: non-planar, *trans-anti* configuration. Dihedral angle between oxime- and amide- groups is ~40° Piperidine-group has chair conformation. Solutions (dmso-d$_6$): *anti*-isomer only; restricted rotation around C-N amide bond; ΔG=64.9 kJ/mol; $T_{(coalescence)}$= 343 K	41a 41a
 HMCO	Solid state: planar, *trans-anti* geometry of the cyanoxime skeleton. Morpholyl-group adopts chair conformation. Seven independent molecules in the unit cell. Solutions (dmso-d$_6$): mixture of *syn*- and *anti*- isomers (1:3), plus restricted rotation around C-N amide bond at 296 K. ΔG=63.7 kJ/mol; $T_{(coalescence)}$=328 K. After 353K exists only *anti*-isomer.	41a 41a
 HPCO	Solid state: non-planar, *cis-anti* geometry. Dihedral angle between planar oxime- and pyridyl- groups is 10.64° Solutions (CDCl$_3$, acetone-d$_6$): *anti*- isomer only at 296K	30b 41b
 HQCO	Solid state: monohydrate; non-planar, *trans-anti* geometry. Dihedral angle between planar oxime- and quinolyl- groups is 10.47° Solutions: *nitroso-oxime* tautomeric equilibrium in polar aprotic solvents (HMPA-d$_{18}$; acetone-d$_6$); *anti*-isomer at 296 K	30b 56
 HBTCO	Solid state: planar structure, *trans-anti* geometry; two independent molecules in the unit cell. Solutions (acetone-d$_6$): mixture of *syn*- and *anti*- isomers (1:3) at 290 K.	29b 31e
 HiTLCO	Solid state: planar *cis-anti* configuration. Solutions (acetone-d$_6$): mixture of syn- and anti- isomers in solutions at 296 K	29c 31e

Table 4. (Continued)

 HSLCO	Solid state: monohydrate; planar *trans-a*nti configuration; two independent molecules in the unit cell. Solutions (dmso-d6): mixture of *syn*- and *anti*- isomers (~3:2) at 298 K	42a 42a
 HTLCO	Solid state: planar, *trans-syn* geometry. Solutions (CD_3CN, acetone-d_6): mixture (~2:3) of *syn*- and *anti*- isomers at room temperature.	30b 30b
 H(3F-PhCO)	Solid state: planar *cis-syn* configuration. Solutions (dmso-d_6): one set of signals in ^{1}H and ^{13}C NMR spectrum; presumably *syn*- conformation at 296 K.	this work
 H(2Cl-PhCO)	Solid state: non-planar *trans-anti* configuration. Dihedral angle between 2-Cl-phenyl and cyanoxime groups is 43°. Solutions (dmso-d_6): one set of signals in ^{1}H and ^{13}C NMR spectra assigned to presumably the most favorable *anti*- configuration	this work
 H(4Cl-PhCO)	Solid state: non-planar *anti*-configuration. Dihedral angle between 4Cl-phenyl and cyanoxime fragments is 18°. Solutions (dmso-d_6): one set of signals in ^{1}H and ^{13}C NMR spectra assigned to *anti*- configuration	this work
 HBCO	Solid state: non-planar *trans-anti* configuration. Solutions (dmso-d_6): one set of signals in ^{1}H and ^{13}C NMR spectra assigned to *anti*- configuration	31e 26a

[a] X-ray single crystals analysis. [b] Data from NMR spectroscopic measurements including, in some cases, variable temperature studies.

density on the N−O bond in the molecule when an anion coordinates to the metal center.

Centrosymmetric dimeric Tl_2L_2 units (L = 2Cl−PhCO) that consist of planar Tl_2O_2 rhombes are connected to the one-dimensional staircase structure by means of the oxygen atom of the oxime group of the neighboring unit, forming infinite columns (Figures 7 and 8). The cyanoxime anion in the structure of Tl(2Cl−PhCO) acts as a bridging ligand and forms a one-dimensional coordination polymer (binding mode **2**, Scheme 3). There are two short and almost equal Tl(1)−O(1) bonds (2.587 and 2.594 Å) inside the rhomb in a dimeric unit and one slightly longer Tl(1)−O(1*) bond (2.803 Å) between the adjacent, at 90.7°, rhombs in the structure of Tl(2Cl−PhCO). Thus, the two intradimeric metal−oxygen distances are ~0.2 Å shorter than the interdimeric Tl−O contact. Several reference sources provide slightly different values of ionic radii for oxygen and thallium(I): 1.40 and 1.54 Å ($\Sigma = 2.94$ Å),[33a] 1.32 and 1.47 Å ($\Sigma = 2.79$ Å),[47] and 1.38 and 1.50 Å ($\Sigma = 2.88$ Å),[70] respectively. Nevertheless, all three Tl−O distances in synthesized Tl(I) arylcyanoximates are shorter than the above sums of ionic radii[39,47] for these elements and, therefore, are considered as bonds. There are two slightly different rhombes, **1** and **2**, in the structure of the complex. The dihedral angle and other geometrical parameters in these rhombes are shown in Figure 9. Thallium(I) ions in the

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(70) Shannon, R. D. *Acta Crystallogr., Sect A* **1976**, *32*, 751−767.

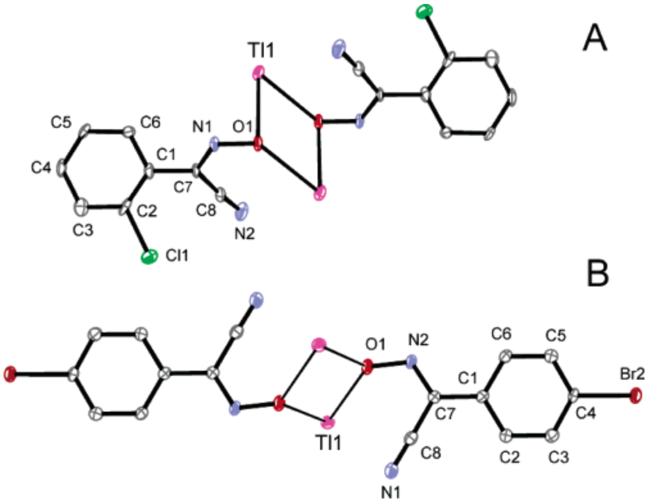


Figure 6. Molecular structures and numbering schemes for centrosymmetric dimers $[Tl(2Cl-PhCO)]_2$ (A) and $[Tl(4Br-PhCO)]_2$ (B), an ORTEP drawing at the 50% probability ellipsoids.

structure form infinite linear arrays aligned along the *x* axis. The shortest Tl···Tl separation in the structure is 3.838 Å, which is only slightly longer than that for metallic thallium ($a = 3.456$ Å). Centrosymmetric dimers $[Tl(2Cl-PhCO)]_2$ pack into a crystal with the formation of a lattice that is stabilized by $\pi-\pi$ stacking interactions between 2-chloroaryl groups (Figure 7). Organization of the crystal structure is shown in Figure 8. The structure of a ruffled Tl_2O_2 rhombes displaying a motif of zigzag sheets is shown in Figure 9.

The geometry of the Tl(I) coordination polyhedron in the structure of the complex is best described as a distorted trigonal pyramid and is displayed in S7 of the Supporting Information. The central atom has a stereoactive lone pair pointed away from the $\pi-\pi$ stacking columns of Tl(2Cl−PhCO) in the open cleft between them. It should be mentioned that the Tl1···N2 contacts have a nonbonding, electrostatic origin due to the improper orientation of the CN group and thallium centers. Thus, angles between the nitrogen atom and the two closest Tl(I) ions are 89.9° and 120°, which is significantly less than expected for the conventional binding angle, ∼180°, in numerous metal−cyanide complexes.

Contrary to our expectations, the ortho chlorine atoms of the aryl group do not support the metal center in the complex by additional coordination, and they do not participate in forming a crystal lattice. The nearest distance, Tl···Cl = 4.186 Å, is beyond any reasonable interaction considered between these two atoms. The closest distance between the chlorine atom and another atom of a neighboring molecule is Cl1···H4 = 3.017 Å, which is the same as the sum of their van der Waals radii (3.00 Å)[47] and may indicate weak interaction between columns of TlL complexes.

2.3. Tl(4Br−PhCO). The molecular structure of this complex is shown in Figure 6B, while bond lengths and valence angles in the structure of Tl(4Br−PhCO) are presented in Table 5. The cyanoximate anion in Tl(4Br−PhCO) is nearly planar and adopts an anti configuration of the oxime group with respect to the 4-bromophenyl group; the dihedral angle between the planar cyanoxime fragment and the aryl group is 9.4°. Interestingly, the configuration and degree of planarity of the cyanoxime in an anion and is almost the same in the structures of H(4Cl−PhCO) and Tl(4Br−PhCO). H(4Cl−PhCO), certainly, is a structurally analogous ligand to H(4Br−PhCO). Bond lengths O1−N2 and N2−C7 of the oxime fragment in the Tl(I) complex are 1.346 and 1.309 Å, respectively, while the same bond lengths in the structure of uncomplexed H(4Cl−PhCO) are 1.378 and 1.289 Å. It is remarkable, however, that the sum of both bond lengths is practically identical: 2.655 Å for Tl(4Br−PhCO) and 2.667 Å for H(4Cl−PhCO) (Tables 3 and 5). Again, differences in bond distances in the oxime group between the ligand and the metal complex reflect a redistribution of the electron density in the C−N−O fragment during complexation to the metal center.

The crystal structure of Tl(4Br−PhCO) is similar to that of Tl(2Cl−PhCO) described above. Thus, the centrosymmetric dimers $[Tl(4Br-PhCO)]_2$ are joined together by oxygen atoms of bridging cyanoxime anions into columns (Figure 10), oriented along the *y* axis. The cyanoxime anion acts as the bridging ligand (binding mode **2**, Scheme 3) using an oxygen atom of the NO group to form Tl_2O_2 rhombes (Figure 6B). The Tl_2O_2 rhombes are connected with a formation of ruffled or zigzag sheets; the dihedral angle between the Tl_2O_2 planar fragments is equal to 99.2°. Two rhombes, **1** and **2**, in the structure have slightly different geometry (Figure 11). All three Tl−O bonds in the structure have very close values, 2.640, 2.640, and 2.687 Å, where the interdimeric distance is ∼0.05 Å longer than the intradimeric contacts. Again, the sum of ionic[47,70] radii for Tl and O is greater than the above distances, which are considered as bonds. The shortest Tl···Tl distance is 4.058 Å and is ∼0.6 Å greater than that in metallic thallium. The crystal structure of the complex represents a double-stranded one-dimensional coordination polymer with infinite, well-aligned linear arrays of close monovalent Tl cations (Figures 10−12).

The structure of the coordination polyhedron in the structure of Tl(4Br−PhCO) can be best described as a distorted trigonal pyramid and is shown in S8 of the Supporting Information. The lone pair of Tl(I) in the structure is stereoactive, directed away from the columns of polymeric Tl(4Br−PhCO) complexes and pointed toward the bromine atoms of neighboring columns in an open cleft.

The $\pi-\pi$ stacking interactions between the 4-bromophenyl groups of neighboring molecules at a distance of 4.058 Å stabilize this elegant structure (Figure 12). It should be mentioned that there are long, additional interactions of an electrostatic nature between Br2 and N1 atoms (nitrile group) and thallium(I) centers (Figure 10). These both intra- and intercolumn interactions provide additional stabilization to the crystal lattice. Also, it is important to note a short, 3.632 Å, Br···Br nonbonding contact in the structure. The Br2−Br2′−Br2 angle between neighboring columns of Tl(4Br−PhCO) is 83°, while the closest distance between bromine atoms in the same π-stack column is 4.058 Å (see the Supporting Information, S9). This intracolumnar Br···Br distance is significantly larger than the intercolumnar separa-

Table 5. Selected[a] Bond Lengths (Å) and Valence Angles (deg) in the Structures of Thallium Complexes

Tl(2Cl−PhCO)				Tl(4Br−PhCO)			
bond length		valence angle		bond length		valence angle	
Tl(1)−O(1)[b]	2.587(13)	O(1)−Tl(1)−O(1)#1	72.3(5)	Tl(1)−O(1)[c]	2.641(2)	O(1)−Tl(1)−O(1)#1	78.23(9)
Tl(1)−O(1)#1	2.594(13)	N(1)−O(1)−Tl(1)	102.3(10)	Tl(1)−O(1)#1	2.640(3)	N(2)−O(1)−Tl(1)	91.16(17)
Cl(1)−C(2)	1.770(18)	N(1)−O(1)−Tl(1)#1	140.0(10)	Br(2)−C(4)	1.903(3)	N(2)−O(1)−Tl(1)#1	123.77(19)
O(1)−N(1)	1.364(18)	Tl(1)−O(1)−Tl(1)#1	107.7(5)	O(1)−N(2)	1.346(4)	Tl(1)−O(1)−Tl(1)#1	101.77(9)
N(1)−C(7)	1.31(2)	C(7)−N(1)−O(1)	114.6(15)	N(2)−C(7)	1.309(4)	C(7)−N(2)−O(1)	116.1(3)
N(2)−C(8)	1.17(3)	C(2)−C(1)−C(7)	124.1(17)	N(1)−C(8)	1.154(5)	C(2)−C(1)−C(7)	120.3(3)
C(1)−C(2)	1.36(3)	C(6)−C(1)−C(7)	117.7(16)	C(1)−C(2)	1.396(5)	C(6)−C(1)−C(7)	120.8(3)
C(1)−C(6)	1.40(3)	C(1)−C(2)−Cl(1)	119.8(14)	C(1)−C(6)	1.403(5)	C(3)−C(4)−Br(2)	118.6(2)
C(1)−C(7)	1.49(2)	N(1)−C(7)−C(8)	120.2(16)	C(1)−C(7)	1.465(5)	N(2)−C(7)−C(8)	118.2(3)
C(7)−C(8)	1.42(3)	N(1)−C(7)−C(1)	118.0(16)	C(7)−C(8)	1.453(5)	N(2)−C(7)−C(1)	121.3(3)
		C(8)−C(7)−C(1)	121.6(16)			C(8)−C(7)−C(1)	120.3(3)
		N(2)−C(8)−C(7)	175(2)			N(2)−C(8)−C(7)	178.5(4)

[a] The geometry of the phenyl group is normal and not shown. [b] There is also a third contact, Tl(1)−O(1)#2 = 2.803(7) Å, that is responsible for the formation of the coordination polymer (Figure 9). [c] The third contact, Tl(1)−O(1)#3 = 2.687(2) Å, provides the addition of the oxygen atom to the Tl_2O_2 rhomb in a dimer, leading to a staircase zigzag sheet (Figure 11).

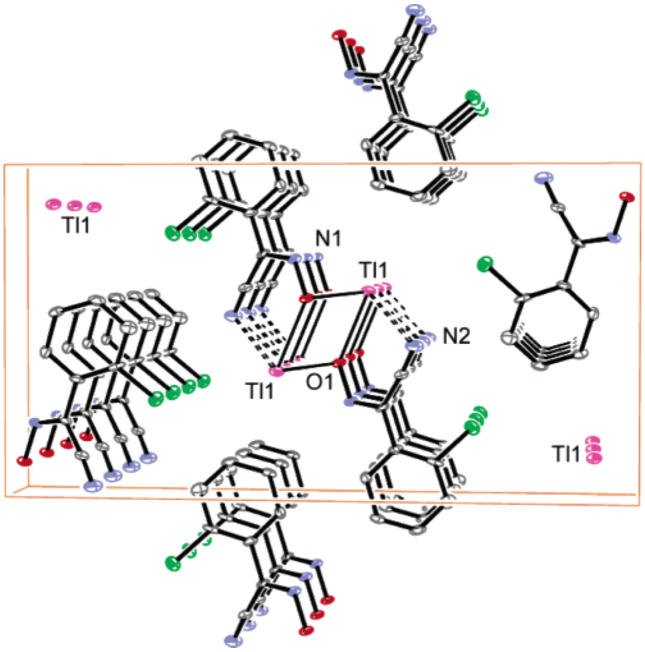


Figure 7. Prospective view of the crystal structure of the Tl(2Cl−PhCO) complex. View along the Tl···Tl direction showing the electrostatic nonbonding Tl1···N2 interactions as dashed lines.

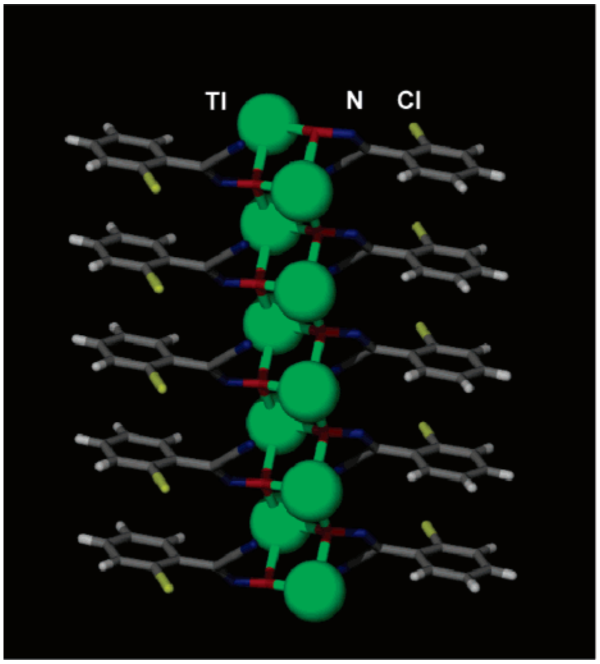


Figure 8. Organization of the Tl(2Cl−PhCO) structure showing formation of the polymeric column with a ruffled Tl_2O_2 rhombes as a zigzag sheet. Thallium(I) ions are green colored.

tion of 3.632 Å. The shorter than the sum of van der Waals radii[39,47] Br···Br distance (3.92 Å) in different compounds is not unusual and, for example, was reported recently[48] in the ladder-type bridging structure of the tetrabromocuprate(II) anion in its pentylammonium salt.

It is interesting to compare the distances between $\pi-\pi$-stacking monosubstituted aryl groups in the structures of both thallium(I) cyanoximates. Thus, the separation between two phenyl rings in Tl(2Cl−PhCO) is 3.838 Å, while the same separation for Tl(4Br−PhCO) is equal 4.058 Å. The difference is 0.22 Å and is very close to the van der Waals radii difference between Cl and Br atoms: 0.15 Å. The presence of π-stacking interactions between haloaryl groups that provide extra stabilization of the crystal lattice in both crystallographically characterized thallium(I) complexes is essential for potential electric conductivity in the crystal.[50] This situation is similar to that for S or Se tetrafulvalenes and their metallocomplex derivatives, where an electric conductivity and low-temperature superconductivity in crystals was observed in the direction perpendicular to the π-stacking columns of planar organic molecules.[51] In principle, electron transport (hopping) between different oxidation states in mixed-valence Tl^+/Tl^{3+} cyanoxime complexes can be achieved through bridging atoms of an NO− group of anions, or via aligned π-stacking monosubstituted aryl groups. To follow the preparation of their mixed-valence complexes, the next step in our investigation is the synthesis and study of Tl(III) complexes with the same set of cyanoxime ligands. In light of the results presented here, synthesis of the unsubstituted phenylcyanoxime, H(PhCO), and its thallium complexes is justified with regard to the closest location of both metal centers and π-stacking aligned phenyl groups. This investigation is in progress, and results will be submitted for publication shortly.

The structures of the two thallium complexes presented in this paper are similar to the staircase polymeric motif in

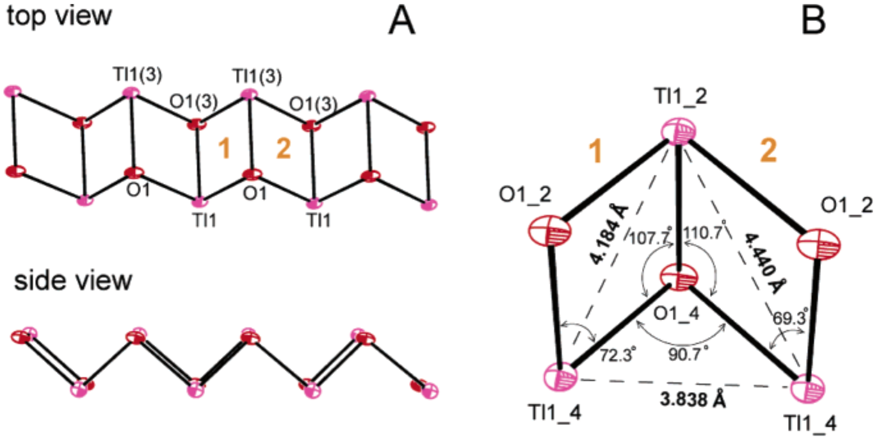


Figure 9. Isolated polymeric Tl−O sheets (A) and the geometry of two adjacent planar Tl_2O_2 diamonds in the structure (B), an ORTEP representation at the 50% probability level.

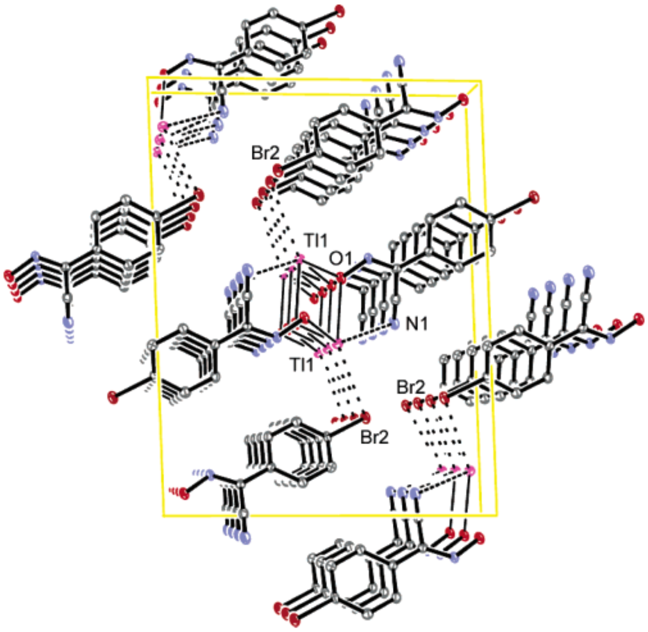


Figure 10. Fragment of the crystal structure of Tl(4Br−PhCO)]. Prospective view along the *y* axis showing the electrostatic nonbonding Tl1···N1 and Tl1···Br2 interactions (dashed lines).

Tl(2-nitrophenolate) reported by Harrowfield et al.[62b] It appears that weak aromatic organic acids such as phenols and oximes might support the formation of such double-stranded one-dimensional polymers stabilized by additional $\pi-\pi$ stacking interactions. Surprisingly, Tl(4-nitrophenolate) is a tetramer and adopts the shape of a distorted cube.[62b] Further investigations are needed to establish correlations between the nature of the ligand and the structure of the obtained Tl(I) complex.

Synthesized Tl(I) cyanoximates all form long needle-type crystals (Supporting Information, S5 and S6), which represents a useful property for future electric conductivity studies.

Experimental Section

Materials and Methods. Starting thallium(I) carbonate and monosubstituted phenylactonitriles $R-CH_2-CN$ were obtained from Aldrich and were of acceptable quality. Generated in the lab on the day of the synthesis of cyanoximes, alkylnitrites were used as nitrosating agents. Synthesized monosubstituted cyanoximes with their commonly used abbreviations are shown in Scheme 4. Melting points for synthesized protonated cyanoximes and their Na and Tl(I) salts were determined in open capillary tubes using the Mel-Temp apparatus (Thomas−Hoover) without correction. An elemental analyses on C/H/N content was performed at the Atlantic Microlab (Norcross, GA) and MicroMass Laboratory at the University of California (Berkeley).

Spectroscopic Methods. All synthesized organic ligands were characterized at 296 K using ^1H and ^{13}C NMR spectroscopy (solutions in DMSO-d_6 and $CDCl_3$ containing TMS as an internal standard; Varian Gemini 200 and Bruker Avance DRX-500). UV−visible spectra were recorded at room temperature on an HP 8354 diode array spectrophotometer in the range 200−1100 nm, using 1 mm and 10 mm quartz cuvettes (from Starna, Inc.). A typical tabulated optical spectroscopy data set is presented in S1 of the Supporting Information for H(2Cl−PhCO) as an example. Infrared spectra were obtained in the range 500−4000 cm^{-1} using the FT IR Nicolet Magna 550 spectrophotometer, equipped with OMNIC software. Spectra of protonated cyanoximes HL and their sodium salts NaL were recorded using KBr pellets. However, the spectra of thallium(I) complexes TlL were obtained from fine suspensions in Nujol because of the solid-state exchange reactions between KBr and TlL during the pellet preparation. Results of IR spectroscopic studies of synthesized arylcyanoximates are summarized in S4 of the Supporting Information. A mass-spectrometric technique (positive FAB) of the protonated monosubstituted arylcyanoximes was carried out using Autospec Q and ZAB Finigan spectrometers. Meta-nitrobenzylic alcohol, NBA, was used as a matrix in all experiments.

X-ray Crystallography. Crystal and molecular structures were determined for three protonated arylcyanoximes and two monovalent thallium complexes. Suitable single crystals of the obtained monosubstituted arylcyanoximes H(2Cl−PhCO), H(3F−PhCO), H(4Cl−PhCO), and Tl(4Br−PhCO) were used for structure determination using a Siemens R3m/V automated diffractometer. Data collection for protonated ligands was carried out at room temperature, and a single crystal of the thallium complex Tl(4Br−PhCO) was cooled to 100 K. Structural studies of Tl(2Cl−PhCO) were conducted at 193 K on a diffractometer equipped with a Bruker Smart CCD area detector. The crystal data and some experimental data for the compounds that were studied are listed in Table 2. More detailed crystallographic information for the analyzed com-

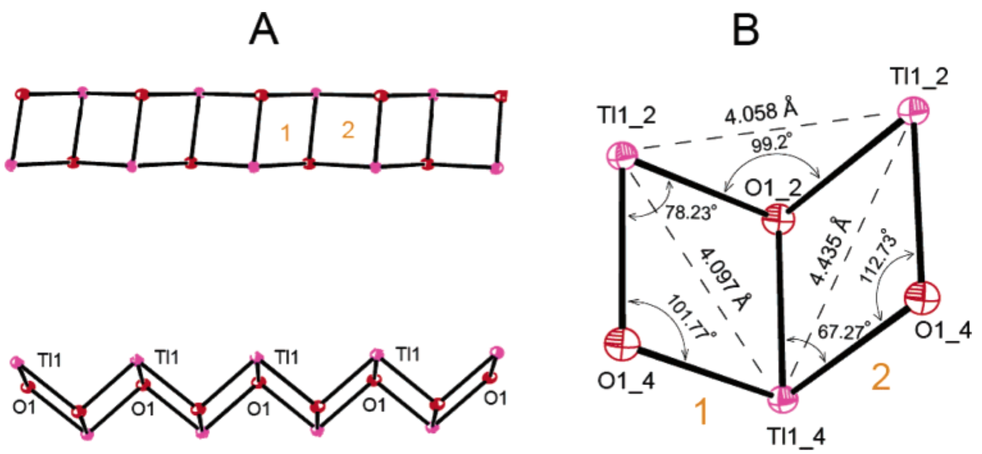


Figure 11. Top and side views of one-dimensional polymeric zigzag sheets in the structure of Tl(4Br−PhCO) (A) and the geometry of two different and adjacent $(Tl1-O1)_2$ rhombes (B) shown at the 50% thermal ellipsoids probability level.

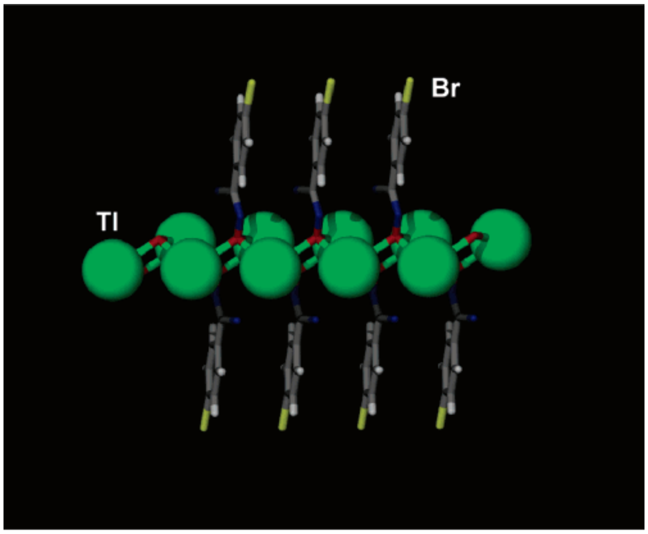


Figure 12. Organization of the one-dimensional coordination polymer in the structure of Tl(4Br−PhCO)] showing π-stacking interactions between aligned 4-bromophenyl groups and ruffled Tl_2O_2 sheets where spatially close Tl(I) atoms form an infinite linear array. Metal ions (green) are presented as balls of the ionic radius size.

pounds is available in the Supporting Information (S11 and respective CIF files).

Synthesis of Monosubstituted Arylcyanoximes. The preparation of these compounds was accomplished using route **3** (modified Meyer reaction[52]), shown in Scheme 6. The first two, most obvious routes, **1** and **2**, represent nitrosation reactions at acidic conditions and were successfully used in previous preparations of other cyanoxime ligands.[22] However, these methods did not work for substituted phenylacetonitriles, which contain a significantly less-activated methylene group. Nitrosating agents such as alkylnitrites (n-C_3H_7−ONO and CH_3−ONO) *must be prepared fresh before use* to avoid possible and, unfortunately, encountered side reactions. The commercial products—amylnitrite and butylnitrites—from Aldrich were of poor quality. Isolated, spectroscopically and structurally characterized examples of the products of the side reactions are shown in the Supporting Information, S10. Small quantities (5−20 g) of methylnitrite or n-propylnitrite were freshly made (according to published procedures[53]) each time prior to use in oxime synthesis reactions. Nitrosation at basic conditions, using freshly prepared alkylnitrites, leads to desired arylcyanoximes with 70−90% yields. Since all preparations of protonated monosubstituted arylcyanoximes are similar, the synthesis of only one ligand will be presented in detail.

Preparation of 2-Fluorophenyl(oximino)acetonitrile, H(2F−PhCO). Metallic sodium in the amount of 0.182 g (7.9×10^{-3} M) was thinly sliced and then dissolved at room temperature in 20 mL of anhydrous 2-propanol under nitrogen protection. Freshly prepared neat propylnitrite, n-C_3H_7−ONO (0.916 g, 8.9×10^{-3} M), was mixed with 1.000 g (7.4×10^{-3} M) of 2-fluorophenyl acetonitrile in 20 mL of anhydrous 2-propanol at room temperature. Nitrogen was passed through this solution for ∼10 min. The latter solution was added dropwise at room temperature within 30 min to a solution of sodium 2-propoxide. The color of the reaction mixture immediately turned yellow, and the mixture remained clear after being stored overnight at 4 °C. The solvent was completely removed using a rotary evaporator and then an oil pump. The yellow solid residue was dissolved in 30 mL of water and then acidified to a pH of ∼5 with the following addition of solid NaCl. This step resulted in a flaky, slightly pale-yellow precipitate of H(2F−PhCO) that was filtered, washed with water, and dried in a vacuum desiccator over P_4O_{10}. An alternative way of cyanoxime recovery is extraction with ether (three portions of 25, 50, and 75 mL each). In this case, ether layers were combined and dried under Na_2SO_4, and the solvent was completely removed, yielding a pale-white solid. The yield of H(2F−PhCO) was 74%. mp = 118 °C. R_f = 0.28 in the 1:4 EtOAc/hexane mobile phase. ^{1}H NMR (ppm): 14.22 (broad singlet, 1H, OH), 7.68 (m, 1H, Ar H), 7.57 (m, 1H, Ar H), 7.38 (m, 1H, Ar H), 7.32 (m, 1H, Ar H). UV−vis (in EtOH; here and elsewhere, 1 mm cell, $\sim 5 \times 10^{-4}$ M): 228 nm ($\epsilon = 7200$), CN group; 302 nm ($\epsilon = 8900$), oximino/aryl fragment. High-resolution mass spectrometry: calcd for $C_8H_5FN_2O$, 164.0386; found, 165.0464 (M + 1).

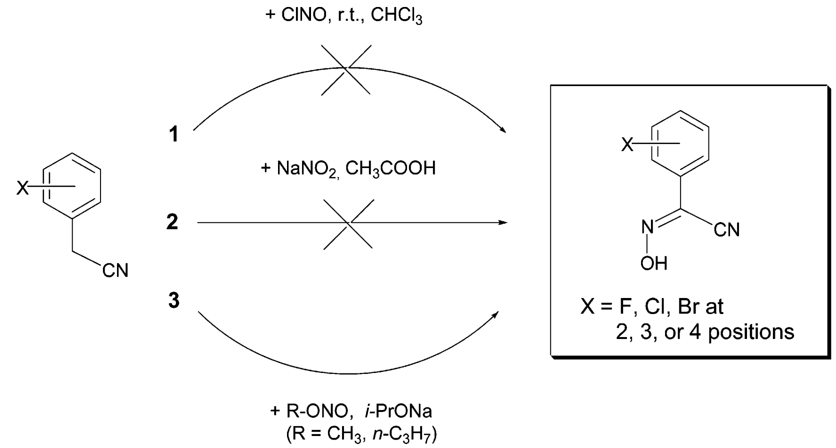
The data for other cyanoximes are presented in the following paragraphs.

H(2Cl−PhCO). Yellow-orange solid, yield 86%. mp = 112 °C. R_f = 0.27 in 1:4 EtOAc/hexane. ^{1}H NMR (ppm): 14.15 (singlet, 1H, OH), 7.49 (m, 1H, Ar H), 7.75 (m, 1H, Ar H), 7.66 (m, 2H, Ar H). UV−vis (in t-BuOH): 220 nm (shoulder), 256 nm (ϵ = 6500).

H(2Br−PhCO). Light-orange solid, yield 85%. mp = 83 °C. R_f = 0.25 in 1:4 EtOAc/hexane. ^{1}H NMR (ppm): 14.52 (singlet, 1H, OH), 7.79 (m, 1H, Ar H), 7.59 (m, 1H, Ar H), 7.54 (m, 1H, Ar H), 7.49 (m, 1H, Ar H). Mass spectrometry (FAB+): calcd for $C_8H_5BrN_2O$, 225.4; found, 226.6 (M + 1).

H(3F−PhCO). White solid, yield 51%. mp = 115 °C. R_f = 0.14 in 1:4 EtOAc/hexane. ^{1}H NMR (ppm): 14.11 (singlet, 1H, OH),

Scheme 6



7.79 (doublet, 1H, Ar H), 7.74−7.18 (m, 3H, Ar H). UV−vis (in methanol): 224 nm ($\epsilon = 8150$), CN group; 304 nm ($\epsilon = 7770$), oximino-aryl fragment.

H(3Cl−PhCO). Pale-yellow solid, yield 68%. mp = 105 °C. $R_f = 0.21$ in 1:4 EtOAc/hexane. ^{1}H NMR (ppm, mixture of two isomers): 14.05 (broad singlet, 2H, OH), 8.04 (m, 1H, Ar H), 7.85 (m, 1H, Ar H), 7.70−7.56 (m, 6H, Ar H). Mass spectrometry (FAB+): calcd for $C_8H_5ClN_2O$, 180.6; found, 181.5 (M + 1).

H(3Br−PhCO). Pale-yellow solid, yield 77%. mp = 109 °C. $R_f = 0.35$ in 1:4 EtOAc/hexane. ^{1}H NMR (ppm): 14.06 (broad singlet, 1H, OH), 7.79 (s, 1H, Ar H), 7.76−7.36 (m, 3H, Ar H). Mass-spectrometry (FAB+): calcd for $C_8H_5BrN_2O$, 225.4; found, 226.6 (M + 1).

H(4F−PhCO). Light-yellow solid, yield 53%. mp = 89 °C. $R_f = 0.20$ in 1:4 EtOAc/hexane. ^{1}H NMR (ppm): 13.82 (broad singlet, 1H, OH), 8.04 (m, 2H, Ar H), 7.51 (m, 2H, Ar H).

H(4Cl−PhCO). Yellow solid, yield 63%. mp = 95 °C. $R_f = 0.26$ in 1:4 EtOAc/hexane. ^{1}H NMR (ppm, mixture of two isomers): 14.12 (broad singlet, 2H, OH), 8.05−7.50 (4 doublets, 8H, Ar H).

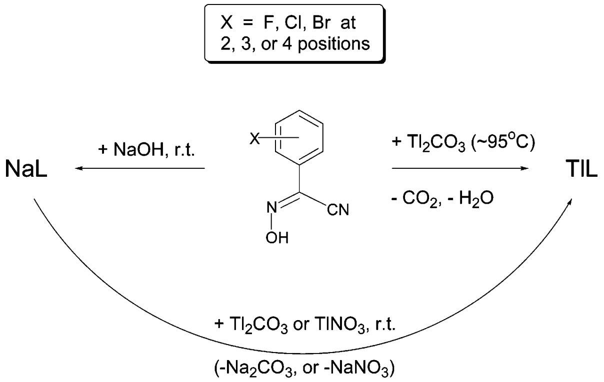
H(4Br−PhCO). Pale-yellow solid, yield 77%. mp = 135 °C. $R_f = 0.27$ in 1:4 EtOAc/hexane. ^{1}H NMR (ppm, mixture of two isomers): 14.0 (broad singlet, 2H, OH), 7.9−7.65 (4 doublets, 8H, Ar H). UV−vis (in ethanol): 220 nm ($\epsilon = 8500$), CN group; 273 nm (7920), aryl fragment.

Synthesized monohalogenated arylcyanoximes represent white or pale-yellow crystalline substances soluble in ether, CH_2Cl_2, $CHCl_3$, CH_3CN, acetone, ethyl acetate, and alcohols; the compounds are insoluble in CCl_4, water, benzene, and hexanes. A complete set of ^{13}C NMR spectra for the rest of the synthesized cyanoximes can be found in the Supporting Information (S1 and S2).

The deprotonation of colorless arylcyanoximes by bases (metal oxides, hydroxides, and carbonates) in aqueous or alcohol solutions at room temperature leads to yellow/orange anionic cyanoximates. A series of sodium salts, NaL, of all monosubstituted halogenated arylcyanoximes described in this paper was obtained and spectroscopically (IR) characterized. A stoichiometric reaction (1:1) between ethanol solutions of HL and freshly prepared aqueous NaOH quantitatively affords yellow powdery NaL, which was filtered and washed with cold EtOH and dried at 40 °C within 24 h using an oil pump.

Synthesis of Monovalent Thallium Complexes. Scheme 7 shows a general approach to the preparation of Tl(I) cyanoximates. The method that involves using a hot Tl_2CO_3 solution is preferred since, after the CO_2 evolution, only pure TlL is left in the reaction vessel without any other ionic species. Slow cooling of the reaction mixture affords needlelike crystals. Many of these crystals were not of X-ray analysis quality. While the method of an ion exchange between NaL (L = 3-substituted arylcyanoximes) and inorganic Tl(I) salts (Scheme 7) results in better quality crystals, it takes much longer. The following preparation of Tl(4Br−PhCO) represents the typical preparation that was employed during this work.

Scheme 7



Preparation of Thallium(I) 4-Bromophenyl(oximino)acetonitrile, Tl(4Br−PhCO). 0.364 g (0.78×10^{-3} M) of Tl_2CO_3 were dissolved in 10 mL of water at 95 °C. 0.350 g (1.56×10^{-3} M) of solid H(4Br−PhCO) were added within 5 min, in small portions under intensive stirring, to a solution of thallium carbonate. The reaction mixture turned yellow, and carbon dioxide evolved. The resulting solution was filtered hot into a long glass tube and left for slow crystallization in a Dewar flask containing 5 L of water at 98 °C. Fibrous yellow crystals were collected by filtration 3 days later, and the mother liquor was left for further crystallization, affording X-ray quality single crystals of Tl(4Br−PhCO). The combined yield was 0.286 g (86%); the complex decomposes at 255 °C. Analogous preparations, as well as the ion-exchange reactions depicted in Scheme 5, led to all nine thallium(I) cyanoximates, which represent the yellow/orange/brown crystalline compounds. The yields, physical properties, and data of the elemental analysis for synthesized complexes are shown in the Supporting Information, S12. The most important IR frequencies for HL, NaL, and TlL (L = monosubstituted arylcyanoximes) are also presented in the Supporting Information, S4. Sodium salts are soluble in cold water, pyridine, DMF, and DMSO. Synthesized thallium(I) cyanoximates are soluble in pyridine, DMF, DMSO, and hot water. Both salts are insoluble in acetone, ether, hydrocarbons and halocarbons, and benzene and its homologues.

Safety Note! *Although we have not encountered any problems during many years of laboratory work and handling, special care should be taken during procedures using thallium compounds because of their toxicity.*[54,55]

Conclusions

A high-yield synthesis of monohalogen-substituted arylcyanoximes was developed using the respective monosubstituted phenylacetonitriles X−Ph−CH$_2$−CN (X = F, Cl, Br at the 2, 3, or 4 positions) and *freshly* prepared methylnitrite under basic conditions at room temperature. Eight out of nine reported cyanoximes were obtained the first time.

Synthesized cyanoximes were characterized using spectroscopic methods (IR, ^{1}H, ^{13}C NMR, UV−visual, and mass spectrometry) and X-ray analysis. The crystal structures of three compounds were determined and revealed rare cases of the coexistence of planar cis−syn and cis−anti isomers in the same crystal for H(3F−PhCO), nonplanar trans−anti for H(2Cl−PhCO), and anti configurations for H(4Cl−PhCO) molecules in the solid state.

All cyanoxime molecules obtained undergo deprotonation with the formation of yellow/orange conjugated anions with charge delocalization. Linear correlations between the positions of a conjugated aryloxime fragment in the UV spectra of solutions of cyanoximate anions in solvents ROH and solvent parameters (pK_a, Z) were established. Pronounced negative solvatochromism in the visible spectra was observed for cyanoximate anions in eight polar protic and aprotic solvents.

All synthesized arylcyanoximes readily form Na$^+$ and Tl$^+$ metal salts, where monovalent thallium quantitatively forms complexes of 1:1 stoichiometry. All nine synthesized Tl(I) complexes form colored crystals of a needle gabitus. The crystal and molecular structures of two thallium(I) complexes were determined and revealed the formation of a double-stranded coordination polymer comprised of Tl···O···Tl zigzag chains making almost orthogonal ruffled Tl$_2$O$_2$ sheets. Tl(I) ions in both complexes are aligned into infinite linear arrays with metal−metal separations close to that in metallic thallium. Crystal structures of the complexes are additionally stabilized by π-stacking interactions between haloaryl groups that are almost perpendicular to the Tl···Tl arrays.

Structurally characterized Tl(I) arylcyanoximates form one-dimensional metal−organic networks completely different from conventional mixed-valence *MX* and *KCP* 1D solids (Scheme 1) or lattices containing traditional bridging halogenides, halcogenides atoms, linear anions such as CN$^-$ and N$_3^-$, or nonlinear conjugated anions N(CN)$_2^-$ and C(CN)$_3^-$.

The obtained monovalent thallium arylcyanoximates represent excellent precursors for mixed-valence Tl$^+$/Tl^{3+} one-dimensional coordination polymers. Formed rigid Tl$_2$O$_2$ zigzag sheets are able to accommodate metal ions in different oxidation states where mixed-valence complexes may show electric conductivity via electron hopping between metal centers in linear arrays of metal ions or through π-stacking haloaryl groups.

Future studies include the preparation and characterization of similar Tl(III) cyanoximates and the synthesis of mixed-valence Tl(I/III) complexes.

Acknowledgment. The authors thank Dr. C. Barnes for his valuable help and encouragement at the beginning of this project and Dr. K. V. Domasevitch for his kind help with resolving the disorder of the oxime group in the structure of fluorinated arylcyanoxime. D.R. is thankful to the SMSU Graduate College and Department of Chemistry for support during the work on this research project. N.G. is very grateful to Jackie Hinton for technical assistance, Dr. Eric Bosch for sharing knowledge of work with the X-Seed program, Dr. Richard Biagioni for helpful discussions, Dr. Chris Barnhard for photos of Tl crystals, and the ACS PRF for financial support (Grant # B-39079-B3).

Supporting Information Available: Results of UV−visible spectroscopic studies of H(2Cl−PhCO), S1; ^{13}C NMR spectra of synthesized arylcyanoximes, S2 and S3; IR spectra of HL, NaL, and TlL (L = arylcyanoxime), S4; photographs of polycrystalline and single-crystal samples of TlL, S5 and S6; coordination polyhedron in Tl(2Cl−PhCO), S7; coordination polyhedron in Tl-(4Br−PhCO), S8; fragment of crystal packing—three layers—of Tl-(4Br−PhCO), S9; encountered side reacted during nitrosation of the arylcyanoximes, S10; X-ray crystallographic details, S11 and S12; elemental content for TlL, S13. Detailed crystallographic information for the analyzed compounds are available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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