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Solubility, Complex Formation, and Redox Reactions in the Tl_2O_3–HCN/CN^-–H_2O System. Crystal Structures of the Cyano Compounds $Tl(CN)_3 \cdot H_2O$, $Na[Tl(CN)_4] \cdot 3H_2O$, $K[Tl(CN)_4]$, and $Tl^I[Tl^{III}(CN)_4]$ and of $Tl^I_2C_2O_4$[†]

Péter Nagy,[‡] Andreas Fischer,[§] Julius Glaser,[§] Andrey Ilyukhin,[||] Mikhail Maliarik,*[,⊥] and Imre Tóth*[,‡]

Department of Inorganic and Analytical Chemistry, University of Debrecen, H-4010 Debrecen Pf. 21, Hungary, Department of Chemistry, Inorganic Chemistry, The Royal Institute of Technology (KTH), S-100 44 Stockholm, Sweden, Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninsky Prospect 31, 119 991 Moscow, Russia, and IFM-Department of Chemistry, Linköping University, S-581 83 Linköping, Sweden

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Thallium(III) oxide can be dissolved in water in the presence of strongly complexing cyanide ions. Tl^{III} is leached from its oxide both by aqueous solutions of hydrogen cyanide and by alkali-metal cyanides. The dominating cyano complex of thallium(III) obtained by dissolution of Tl_2O_3 in HCN is $[Tl(CN)_3(aq)]$ as shown by ^{205}Tl NMR. The $Tl(CN)_3$ species has been selectively extracted into diethyl ether from aqueous solution with the ratio $CN^-/Tl^{III} = 3$. When aqueous solutions of the MCN ($M = Na^+, K^+$) salts are used to dissolve thallium(III) oxide, the equilibrium in liquid phase is fully shifted to the $[Tl(CN)_4]^-$ complex. The $Tl(CN)_3$ and $Tl(CN)_4^-$ species have for the first time been synthesized in the solid state as $Tl(CN)_3 \cdot H_2O$ (**1**), $M[Tl(CN)_4]$ (M = Tl (**2**) and K (**3**)), and $Na[Tl(CN)_4] \cdot 3H_2O$ (**4**) salts, and their structures have been determined by single-crystal X-ray diffraction. In the crystal structure of **1**, the thallium(III) ion has a trigonal bipyramidal coordination with three cyanide ions in the equatorial plane, while an oxygen atom of the water molecule and a nitrogen atom from a cyanide ligand, attached to a neighboring thallium complex, form a linear O–Tl–N fragment. In the three compounds of the tetracyano–thallium(III) complex, **2**–**4**, the $[Tl(CN)_4]^-$ unit has a distorted tetrahedral geometry. Along with the acidic leaching (enhanced by Tl^{III}–CN^- complex formation), an effective reductive dissolution of the thallium(III) oxide can also take place in the Tl_2O_3–HCN–H_2O system yielding thallium(I), while hydrogen cyanide is oxidized to cyanogen. The latter is hydrolyzed in aqueous solution giving rise to a number of products including $(CONH_2)_2$, NCO^-, and NH_4^+ detected by ^{14}N NMR. The crystalline compounds, $Tl^I[Tl^{III}(CN)_4]$, $Tl^I_2C_2O_4$, and $(CONH_2)_2$, have been obtained as products of the redox reactions in the system.

Introduction

In contrast to general assumptions based on the standard reduction potentials of the Tl^{3+}/Tl^+ ($E° = 1.25$ V)[1] and $(CN)_2/CN^-$ or $(CN)_2$/HCN ($E° = 0.27$ and 0.37 V for CN^- and HCN, respectively)[2,3a] redox couples, it has been shown that thallium(III) forms kinetically stable cyanide complexes in aqueous solution.[4] Reduction of thallium(III) to thallium(I) is found to be limited in the solutions under studied conditions (50 mM thallium, CN/Tl $\leq$ 6, high acidity, room temperature) during a period of 1 year, but it is increased for CN/Tl $>$ 6 and pH $>$ 4.[4] This is in accordance with the results of Penna-Franca and Dodson, who have observed a

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* To whom correspondence should be addressed. E-mail: misha@ifm.liu.se (M.M.); imretoth@delfin.klte.hu (I.T.).

[†] Dedicated to Prof. Ernõ Brücher on his 70th birthday.

[‡] University of Debrecen.

[§] The Royal Institute of Technology (KTH).

[||] Russian Academy of Sciences.

[⊥] Linköping University.

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drastic increase of the rate of the $Tl^{III}-Tl^{I}$ exchange reaction with increasing CN^- concentration.[5] In contrast to Tl^{III}, Tl^{I} does not form complexes with cyanide.[6]

The soluble complexes with composition $[Tl^{III}(CN)_n(aq)]^{(3-n)+}$ ($n = 1-4$) can be formed by addition of NaCN to the acidic aqueous solution of $Tl(ClO_4)_3$ and adjusting the CN^-/Tl^{3+} ratio by changing the pH.[4] Formation constants of these species are larger than any other known thallium(III) complexes with monodentate ligands.[4] Structural information on the $[Tl^{III}(CN)_n(aq)]^{3-n}$ species in aqueous solution has been obtained from a combination of XAFS, LAXS, and vibrational spectroscopy techniques.[7a] These data show that the $[Tl(CN)_4]^-$ species is tetrahedral, while the monocyano and biscyano complexes are pseudooctahedral with water molecules filling coordination sites in the thallium polyhedra. The structure of the triscyano complex is less ambiguously defined; it is probably pseudotetrahedral, $Tl(CN)_3(H_2O)$. Both the interatomic Tl−C distances and the corresponding force constants indicate strong covalent bonding between thallium and carbon atoms. Comparison of the Tl−X bond characteristics in the $Tl^{III}X_n^{3-n}$ ($X = Cl^-, Br^-, CN^-$) species with the same number of ligands (n) shows that the $Tl^{III}-CN$ bond is the strongest one.[7a]

Since the establishment of stable and strong $Tl^{III}-CN$ bonding, a number of heteroligand cyano complexes of thallium(III) have been prepared and structurally characterized in the solid state. The notable examples include $Na_2[Tl(edta)CN]\cdot 3H_2O$,[8a] [Tl(tpp)CN],[8b] and $[Tl(en)_2CN](ClO_4)_2$.[8c] Surprisingly, no solid-state structures of homoligand $Tl(CN)_4^-$ and $Tl(CN)_3$ species have been yet reported. The only known homoligand thallium cyanide is a compound with composition $Tl_2C_4N_4$ or "$Tl(CN)_2$" in solid state, which has been prepared in 1871 by Fronmuller by direct interaction between thallium(III) oxide and hydrocyanic acid.[9] Although no examination of the crystal structure of the compound has been reported, it is assumed to be the mixed valence $Tl^{I}Tl^{III}(CN)_4$ rather than to contain Tl^{II}.[3] No attempts to reproduce the preparation and solve the crystal structure of the compound have been reported. Recently, the "$Tl(CN)_2$" compound was prepared by an anhydrous synthetic procedure via reaction of $TlCl_3$ with a stoichiometric amount of $(CH_3)_3SiCN$ in ether.[10] On the basis of X-ray diffraction pattern and IR spectra, the compound was assigned the formula $Tl^{I}Tl^{III}(CN)_4$ as well.

In the present paper we describe alternative routes for preparation of thallium(III) cyanide species in solution. The $[Tl(CN)_n(aq)]^{3-n}$ complexes can be obtained by a direct dissolution of thallium(III) oxide in aqueous solutions of either hydrogen cyanide or alkaline metals cyanides. For the first time $Tl(CN)_3\cdot H_2O$ and $MTl(CN)_4$ compounds ($M = Na^+, K^+$, and Tl^+) have been synthesized and their crystal structures determined. Along with formation of $[Tl(CN)_n(aq)]^{3-n}$ species, the reaction between Tl_2O_3 and aqueous HCN results in intensive redox processes enhanced strongly by the oxide. The oxidation of CN^- in heterogeneous (solution/solid) systems studied in this work may have some environmental impact related to the cyanide-leaching still intensively used in gold-mining.[11]

Experimental Section

Safety Note. Hydrogen cyanide is a highly poisonous compound and should only be handled in a good ventilated hood with extreme care.[12a,b] The toxicity of thallium and its compounds has been previously discussed.[12c]

Reagents. Reagent grade chemicals Tl_2O_3 (99.5%, Strem Chemicals, Inc.), NaCN (Aldrich), and KCN (Aldrich) were used for preparations. Hydrogen cyanide was prepared by a standard method via the reaction between aqueous solutions of NaCN and H_2SO_4 followed by distillation of HCN.[13] Concentrated (1.2 M) aqueous solution of $Tl(ClO_4)_3$ in 4.9 M $HClO_4$ was obtained by anodic oxidation of $TlClO_4$ and analyzed as described previously.[4,14]

$Tl^{III}-CN^-$ Solutions. (A) Aqueous solutions of thallium(III) cyanide species were prepared by addition of aliquots of aqueous solutions of freshly prepared hydrocyanic acid ([HCN] = 0.3−5.0 M) to thallium(III) oxide (a water suspension of 0.21 g of Tl_2O_3; $HCN/Tl_2O_3 \geq 6$). Alternatively, some solutions were prepared by dropwise condensation of the freshly prepared hydrogen cyanide to a water suspension of Tl_2O_3 ($HCN/Tl_2O_3 \geq 6$) under continuous stirring in a cooled flask (NaCl−ice bath) supplied with a water condenser. The mixtures were then kept at room temperature and under vigorous stirring. Reaction time was varied from several minutes to several days depending on required thallium concentration in solution. Undissolved excess of Tl_2O_3 was filtered off.

(B) Aqueous solutions of a $[Tl(CN)_4]^-$ complex were prepared by dissolution of thallium(III) oxide (0.14 g) in aqueous solutions of either potassium or sodium cyanide ($[CN^-] = 0.3-0.6$ M; $CN^-/Tl_2O_3 \geq 8$). The mixtures of Tl_2O_3 and aqueous solutions of MCN ($M = Na^+, K^+$) were stirred continuously during time intervals from several hours to several days followed by filtration of undissolved Tl_2O_3.

(C) The $Tl^{III}-CN^--H_2O$ solutions were also prepared by addition of a calculated volume of a sodium cyanide solution to the stock solution of thallium(III) perchlorate as described previously.[4]

(D) Water-saturated solutions of a $Tl(CN)_3$ complex in diethyl ether were obtained by extraction from the $Tl^{III}-CN^--H_2O$ solutions containing the $Tl(CN)_3$ species as a dominating complex to the equal volume of the organic solvent followed by separation of the phases. The aqueous solution of $Tl(CN)_3$ ($[Tl^{III}] = 0.5$ M,

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[CN^-] = 1.5 M; pH = 5) was prepared by dropwise addition of a freshly prepared NaCN solution to the $Tl(ClO_4)_3$ stock solution under vigorous stirring. The pH was adjusted by addition of a calculated amount of fresh NaOH.

Synthesis of Crystals. $Tl(CN)_3 \cdot H_2O$ (1). Plate-shaped single crystals of the compound were obtained by slow evaporation of the solution D placed in a thin glass tube. The crystals are very unstable and rapidly decompose in air forming brown Tl_2O_3.

$Tl^I[Tl^{III}(CN)_4]$ (2). The freshly prepared hydrogen cyanide (obtained from 5.2 g of NaCN) was condensed dropwise to a suspension of thallium(III) oxide (8.3 g) in water (20 mL) under continuous stirring in a cooled flask (NaCl−ice bath) supplied with a water condenser. The mixture was then stirred during 5 days at room temperature. Undissolved Tl_2O_3 was filtered, and colorless plate-shaped crystals of $Tl^I[Tl^{III}(CN)_4]$ were grown both by slow evaporation of the solution in a vacuum desiccator over silica gel and by mixing the solution with diethyl ether followed by cooling the mixture at ∼ +5 °C. In the modified procedure, stirring of the mixture was terminated after 15−20 h, after which pH (and [CN^-]) in the filtrate was artificially increased (to ∼10.5) by addition of NaCN (0.12 g) to shift the equilibrium between the $[Tl(CN)_n(aq)]^{3-n}$ species to the $[Tl^{III}(CN)_4]^-$ complex (vide infra). Analysis of the solution showed that concentrations of the Tl^I and $[Tl^{III}(CN)_4]^-$ species were approximately equal, ∼0.3 M. Alternatively, the same crystal phase can be prepared by slow evaporation of the solution D previously dehydrated by lengthy stirring the solution with $MgSO_4$. Anal. Calcd for $Tl^ITl^{III}C_4N_4$: Tl_Σ, 79.8; Tl^I, 39.9; Tl^{III}, 39.9. Found: Tl_Σ, 78.4; Tl^I, 39.5; Tl^{III}, 38.9. ^{205}Tl NMR (H_2O): $\delta = 2987$ ppm ($[Tl(CN)_4]^-$), $\delta = 8$ ppm (Tl^+).

$K[Tl(CN)_4]$ (3). The procedure of preparing crystals of $K[Tl(CN)_4]$ has previously been described.[5] We have used an alternative way to prepare the crystals either by slow evaporation of the solution B in a vacuum desiccator over silica gel or by mixing the solution with diethyl ether followed by cooling the solution at ∼ +5 °C. Anal. Calcd for $KTlC_4N_4$: K, 11.3; Tl, 58.8. Found: K, 10.7; Tl, 58.0. ^{205}Tl NMR (H_2O): $\delta = 2992$ ppm ($[Tl(CN)_4]^-$).

$Na[Tl(CN)_4] \cdot 3H_2O$ (4). Solution D was allowed to evaporate in a wide-necked weighing bottle until about 10% (by volume) of the solution was left. The bottle was closed and cooled at ∼ +5 °C. Large (up to 2 mm × 2 mm × 0.2 mm) plate-shaped transparent crystals of the compound were obtained after 2 days. The crystals decompose slowly (∼4−7 days) both in air and when sealed in a glass capillary.

$Tl^I_2C_2O_4$ (5). After complete condensation of HCN to the suspension Tl_2O_3−H_2O (2.46 g of Tl_2O_3 and 15 mL of H_2O; HCN/Tl_2O_3 = 6), 5 mL of water was added to the mixture and it was then stirred during 7 days at 70 °C. The undissolved Tl_2O_3 was filtered. Large transparent crystals were formed within a few hours at room temperature. Anal. Calcd for $Tl_2C_2O_4$: Tl, 82.3. Found: Tl, 81.5. IR (NaCl; $\nu(C_2O_4^{2-})$, cm^{-1}): 1634 (s), 1290 (s), 754 (s), 526 (s). ^{205}Tl NMR (H_2O): $\delta = 64$ ppm (Tl^+).

Analyses. The analytical methods for determination of the Tl^I and Tl^{III} concentrations in the solutions were described previously.[4,7] Presence of unreacted HCN in the Tl_2O_3−HCN−H_2O systems affects analytical determination of Tl^I by redox titration with $KBrO_3$. Reliable results on thallium concentrations in the solutions can only be obtained after an oxidation of HCN. The content of Tl^I and Tl^{III} in the thallium cyanide solutions obtained from the Tl_2O_3−HCN−H_2O systems was determined from measurements of peak integrals in ^{205}Tl NMR spectra. The metal content in the solid compounds was determined by ICP-atomic emission spectroscopy. The pH values were measured by a combination electrode (Radiometer GK2401B) connected to a pH meter (Radiometer PHM62 or PHM84).

NMR Measurements. NMR spectra were recorded with Bruker AM400 and Avance 360[15a] spectrometers at a probe temperature of 25 (±0.5) °C. Information on typical ^{205}Tl and ^{13}C NMR parameters for similar systems has been given in recent publications from this laboratory.[4,7] For the quantitative measurements of the ^{205}Tl signal intensities, a 30° flip angle was used with the delay between pulses of 1 s ($\geq T_1$ for the slowest relaxing cyano complex, $[Tl^{III}(CN)_4]^-$). ^{14}N NMR chemical shifts were referenced to a signal of NH_4^+ (5 M NH_4NO_3 solution in 2 M aqueous HNO_3), used as an external standard, taken as −359.6 ppm from liquid CH_3NO_2.[15b]

Single-Crystal and Powder X-ray Analyses. The data of **1** were collected on a KappaCCD diffractometer using λ (Mo Kα, 0.710 73 Å). The data collection for the crystals **2**−**5** was performed on an Enraf-Nonius CAD4 diffractometer using λ (Mo Kα, 0.710 73 Å). Selected crystallographic and experimental data together with the refinement details are given in Table 1. The structures **1**, **3**−**5** were solved by direct methods. Anisotropic displacement parameters were refined for all atoms in the structures.

Diffraction data of **2** were obtained from both single crystals (Enraf-Nonius CAD4 diffractometer, $\lambda = 0.710\,73$ Å (Mo Kα)) and powder (Philips PW 1710 diffractometer, $\lambda = 1.540\,60$ Å (Cu Kα_1, germanium monochromator)), cf. Tables 1 and S1, respectively. The diffraction data could be indexed in cubic system ($a = 7.575$ Å). The structure was refined ($R_1 = 0.02$) in space group $Fm\bar{3}m$ with atomic coordinates: Tl 0 0 0, N $^1/_4$ $^1/_4$ $^1/_4$, C $^1/_6$ $^1/_6$ $^1/_6$ (occupancy $^1/_4$).

The similarity of the crystal structures of **2** and **3** (vide infra), as well as the disorder in the structure of **2**, allowed us to suppose that it had been determined in a sublattice. Closer investigation of the diffraction pattern exhibited weak overstructure reflections in one direction. Doubling of this axis leads to a tetragonal structure ($I4_1/a$). The duplication of the structure is caused by the ratio between the unit cell sides, c/a, of 2, special positions of thallium atoms in the structure of $Tl^I[Tl^{III}(CN)_4]$, and practically identical scattering factors of both Tl^I and Tl^{III}. All this results in the appearance of nonsystematic absences for $l = 2n + 1$. Thus, for example, the relative intensity of the strongest reflection with odd l (−1 2 1) is only 0.3%. Attempts to refine the structure in the true (tetragonal) system resulted in instability of the refinement for both positional and thermal parameters for carbon and nitrogen atoms. Because of this, the results of the refinement are not presented here.[16] The powder diffraction data were also indexed in the tetragonal system, and the cell parameters were refined (Table 1). The observed and calculated diffraction patterns are in good agreement (cf. Table S1).

Results and Discussion

I. Dissolution of Thallium(III) Oxide. 1. Hydrocyanic Acid. The solubility of thallium(III) oxide in water (pH = 7) is very low; the solubility product is 2.5×10^{-47} (20 °C).[17]

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(15) (a) When measuring ^{205}Tl spectra on the Avance 360 spectrometer, the *x*-channel of the BB probe of a 500 MHz spectrometer was tuned to 173.4 MHz. (b) Mason, J. *Nitrogen*; Mason, J., Ed.; Plenum Press: New York, 1987; pp 335−368.

(16) Refinement of the structure in the tetragonal system ($I4_1/a$) resulted in unreliable interatomic Tl−C and C−N distances. Thus, the latter bond length was found to be 1.7 Å which is much longer than that expected for the cyano group (∼1.15 Å); see, for example, ref 2.

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Table 1. Crystal Data and Structure Refinement for $Tl(CN)_3 \cdot H_2O$ (**1**), $Tl^I[Tl^{III}(CN)_4]$ (**2**), $K[Tl(CN)_4]$ (**3**), $Na[Tl(CN)_4] \cdot 3H_2O$ (**4**), and $Tl_2C_2O_4$ (**5**)

empirical formula	$C_3H_2N_3OTl$ (**1**)	$C_4N_4Tl_2$ (**2**)[a]	C_4KN_4Tl (**3**)	$C_4H_6N_4NaO_3Tl$ (**4**)	$C_2O_4Tl_2$ (**5**)
formula weight	300.4	512.82	347.55	385.49	496.76
temperature, K	200	295(2)	295(2)	293(2)	296(2)
wavelength, Å	0.7107	0.71073	0.71073	0.71073	0.71073
crystal system	orthorhombic	tetragonal	tetragonal	monoclinic	monoclinic
space group	*Cmca*	$I4_1/a$	$I4_1/a$	$C2/c$	$P2_1/c$
unit cell dimensions, Å	$a = 10.5729(7)$ $b = 8.0012(7)$ $c = 17.765(1)$	$a = 7.5753(13)$ $c = 15.142(2)$	$a = 7.5470(9)$ $c = 14.987(2)$	$a = 10.6136(11)$ $b = 10.7203(14)$ $c = 19.161(2)$	$a = 6.6141(9)$ $b = 5.8404(11)$ $c = 6.6620(15)$
deg				$\beta = 96.96(2)$	$\beta = 99.22(2)$
volume, Å^3	1502.8(2)	868.9(4)	853.62(18)	2164.1(4)	254.02(8)
Z	8	4	4	8	2
density (calcd), Mg/m^3	5.276		2.704	2.366	6.495
absorption coefficient, mm^{-1}	21.414		19.341	14.950	63.265
crystal size, mm^3	0.15 × 0.15 × 0.01		0.12 × 0.08 × 0.08	0.12 × 0.12 × 0.02	0.20 × 0.15 × 0.12
reflections collected	908		1121	3232	1233
refinement method			full-matrix least-squares on F^2		
data/restraints/parameters	908/0/44		1121/0/24	2258/0/119	1233/0/37
goodness-of-fit on F^2	1.043		0.948	1.092	1.023
final R indices [$I > 2\sigma(I)$]	R1 = 0.0210 wR2 = 0.0318		R1 = 0.0583 wR2 = 0.0973	R1 = 0.0439 wR2 = 0.1109	R1 = 0.0511 wR2 = 0.1170
R indices (all data)	R1 = 0.0352 wR2 = 0.0343		R1 = 0.1460 wR2 = 0.1130	R1 = 0.0595 wR2 = 0.1199	R1 = 0.0553 wR2 = 0.1173
extinction coefficient	0.00039(4)		0.0012(5)	0.0036(2)	

[a] See ref 16 and Experimental Section for details; $a = 7.562(6)$ Å, $c = 15.168(11)$ Å^3, $V = 867.5(16)$ Å^3 from X-ray powder diffraction data.

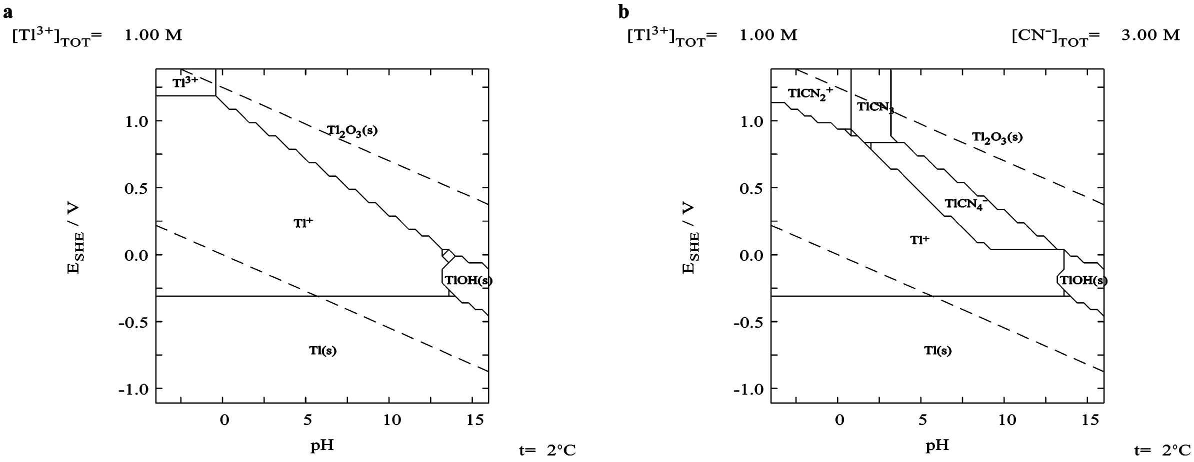

Figure 1. Predominance area (Pourbaix) diagram for $Tl_2O_3-H_2O$ (a) and $Tl_2O_3-HCN-H_2O$ (b) systems. The diagrams were calculated based on formation (stability) constants of the species from refs 4, 18, and 36. Oxidation of cyanide is not taken into account for the $Tl_2O_3-HCN-H_2O$ system.

Inspection of the Pourbaix diagram for thallium (cf. Figure 1a) suggests that there are two obvious ways to dissolve the oxide, which include acidic (1) and reductive (2) dissolution. The former pathway can be realized by dissolution of the oxide in an acid:

$$Tl_2O_3(s) + 6H_3O^+(aq) \rightleftharpoons 2Tl^{3+}(aq) + 9H_2O(l) \qquad \log K = 4.3^{18} \quad (1)$$

The second reaction becomes competitive and can be even dominating in aqueous solutions containing reducing agents:

$$Tl_2O_3(s) + 4e^- + 6H_3O^+(aq) \rightleftharpoons 2Tl^+(aq) + 9H_2O(l) \qquad E° = 1.19\ V^{18} \quad (2)$$

As one can see from Figure 1a, the oxidizing power of the oxide increases with increase of acidity, and reduction of trivalent thallium can be thermodynamically very efficient.

The thallic ion, Tl^{3+}, appears only in media that are both very acidic and very oxidizing (cf. Figure 1a). It is clear that only strong mineral acids ($HClO_4$, HNO_3, H_2SO_4), whose conjugate bases cannot be oxidized by the thallic ion, can be employed to avoid its reduction to the thallous ion, Tl^+, according to the redox reaction:

$$Tl^{3+}(aq) + 2e^- \rightleftharpoons Tl^+(aq) \qquad E° = 1.25\ V^1 \quad (3)$$

The solubility equilibria may be greatly altered further as soon as complexing ions or molecules are present in solution. From the acids listed above, it is only the perchlorate anion which is "innocent"; the thallic ion is present in form of a $[Tl(H_2O)_6]^{3+}$ species in solutions of $HClO_4$.[7] Solutions of thallium(III) in the other acids have been shown to contain complexes with stabilities strongly depending on the complexing anions.[12c,3b,19]

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The extent and the rate of dissolution of an oxide in an acid are generally strongly enhanced if the metal ion can form stable complexes with the conjugate base.[20] In the case of thallium(III) oxide, such a dissolution/complex formation process can be in general case represented as the following:

$$Tl_2O_3(s) + 6HX(aq) \rightleftharpoons 2[TlX_3(aq)] + 3H_2O(l) \qquad (4)$$

emphasising formation of the most dominant tris-complex at the current HX/Tl_2O_3 ratio of 6 ($HX/Tl^{III} = 3$). HCN is a very weak acid ($pK_a = 9.2$ at 25 °C);[2,21,22] however, Tl^{III} forms very stable complexes with CN^- (e.g., $\log \beta_3 = 35.2$ for the $[Tl(CN)_3(aq)]$ complex at 25 °C).[4] This allows us to expect that thallium(III) oxide can be dissolved in hydrocyanic acid, with a driving force being the formation of the $[Tl(CN)_n(aq)]^{3-n}$ ($n = 1-4$) species. Figure 1b shows the Pourbaix diagram of the system in the presence of cyanide ions. One can see that the predominance area of the oxide decreases significantly because of the formation of stable and soluble thallium(III)−cyano complexes.

On the other hand, taking into account a low reduction potential of the $(CN)_2$/HCN couple ($E° = 0.37$ V),[2] a highly thermodynamically favorable reductive dissolution of the oxide should be expected as well:

$$Tl_2O_3(s) + 4HCN(aq) + 2H_3O^+(aq) \rightleftharpoons 2Tl^+(aq) + 2(CN)_2(aq) + 5H_2O(l) \qquad (5)$$

Indeed, when taking into consideration oxidation of cyanide, the Pourbaix diagram does not show any thallium(III) species except $Tl^{3+}(aq)$.

In view of high kinetic stability of the thallium(III)−cyano complexes (vide supra), however, it seems possible that dissolution of Tl_2O_3 in HCN results in formation of the metastable $[Tl(CN)_n(aq)]^{3-n}$ species. Below, we present experimental results verifying the availability of both acidic and reductive pathways for the dissolution of thallium(III) oxide in aqueous hydrogen cyanide.

Figure 2 shows a time dependence of the fraction of dissolved oxide, $f(t)$, for the Tl_2O_3−HCN−H_2O systems. One can see that hydrocyanic acid reacts very effectively with Tl_2O_3. Even when using the diluted acid (∼0.3 M) and $HCN/Tl_2O_3 = 6$, up to 90% of the oxide can be dissolved within 4−6 h at room temperature. Increase of the molar ratio HCN/Tl_2O_3 in the system accelerates the rate of dissolution significantly. Thus for the $HCN/Tl_2O_3 = 12$ the same conversion can be reached within 1−2 h.[23] When we vary the HCN/Tl_2O_3 ratio and/or concentration of the acid, up to 1 M total concentration of thallium in solution can be easily obtained. When using $HCN/Tl_2O_3 = 6$ and terminating the reaction after 8 h (when the reaction is essentially completed, cf. Figure 2), the fraction of the aqueous Tl^+ ion has never exceeded 5−7% of the total concentration of thallium in solution. However, the content of the thallous ion in solution has been substantially higher with increase of the HCN/Tl_2O_3 ratio and/or increase of concentration (vide infra).

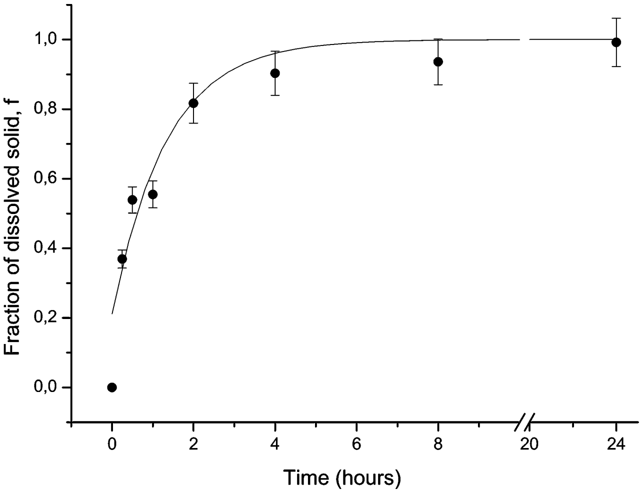

Figure 2. Time dependence of the fraction of dissolved oxide, $f(t)$, for the Tl_2O_3−HCN−H_2O system. Molar ratio $HCN/Tl_2O_3 = 6$, $[HCN] = 0.31$ M; $f = (W_0 - W)/W_0$, where W_0 and W are the initial and the unreacted mass of oxide remaining at time t, respectively.

The pH of the solutions obtained from the Tl_2O_3−HCN−H_2O system varied with the reaction time. It is important to note that in all cases acidity of the solutions obtained by the reaction between the oxide and hydrocyanic acid was higher than for the corresponding aqueous solutions of the pure acid at given concentrations. Thus, the pH of the solutions obtained by the reaction of 0.3 M HCN with Tl_2O_3 ($HCN/Tl_2O_3 = 6$) was 2.9 after 15 min. The pH rose to 3.5 after 8 h of stirring the mixture when dissolution was completed. At the same time, the pH of the 0.3 M aqueous HCN was 4.9. A drastic drop of the pH of aqueous solutions of hydrogen cyanide in the case of reaction with thallium(III) oxide could be attributed to formation of the tetracyano species,

$$[Tl(CN)_3(aq)] + HCN(aq) + H_2O(l) \rightleftharpoons [Tl(CN)_4]^- + H_3O^+(aq) \qquad (6)$$

which is present in the solution in equilibrium with the dominating triscyano complex (vide infra).

I.2. Aqueous Solutions of MCN (M = Na, K). High solubility of thallium(III) oxide in acidic aqueous solutions containing the complexing CN^- ion indicates that some leaching can occur even when using aqueous solutions of alkaline metals cyanides, MCN ($M = Na^+, K^+$). Indeed, stirring of Tl_2O_3−KCN−H_2O mixtures ($[CN^-] = 0.4$ M, $CN^-/Tl_2O_3 = 8$) for 12 h at room temperature results in dissolution of ∼8% of the oxide. Because of the strong basicity of aqueous solutions of MCN (e.g., pH = 11.4 for 0.4 M KCN), one can expect that the dissolution is substantially slower compared to the Tl_2O_3−HCN−H_2O system. Nevertheless, up to 0.03 M concentration of the $[Tl(CN)_4]^-$ complex, a dominant species at these pH and

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(20) Blesa, M. A.; Morando, P. J.; Regazzoni, A. E. *Chemical Dissolution of Metal Oxides*; CRC Press: Boca Raton, FL, 1994.

(21) The pK_a of the acid was shown to be very dependent on the ionic medium. It increases from 9.1 to 10.1 with increase of the ionic medium from 1.00 M $NaClO_4$ to 1.00 M $NaClO_4$−3.00 M $LiClO_4$, respectively.[22]

(22) Bányai, I.; Blixt, J.; Glaser, J.; Tóth, I. *Acta Chem. Scand.* **1992**, *46*, 138.

(23) A detailed study of the kinetics of the dissolution of thallium(III) oxide in aqueous solutions of hydrocyanic acid is outside the scope of this paper.

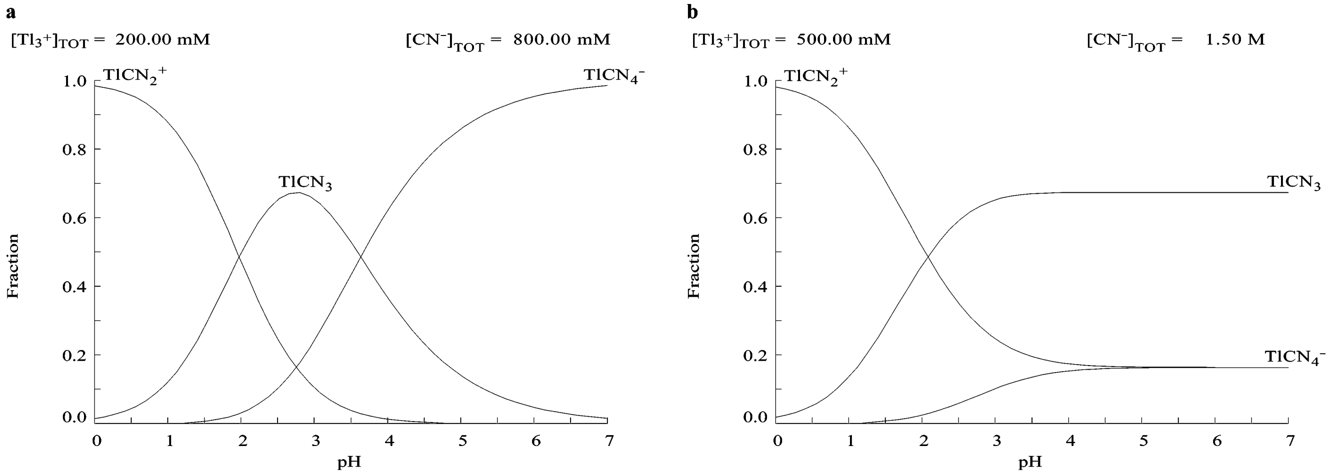

Figure 3. Fraction diagram of the $[\mathrm{Tl(CN)}_n(\mathrm{aq})]^{3-n}$ complexes in aqueous solution as a function of pH, based on the stability constants of the complexes from ref 4 and calculated for the following concentrations: (a) $[\mathrm{Tl^{III}}]_{\mathrm{tot}} = 0.200$ M and $[\mathrm{CN^-}]_{\mathrm{tot}} = 0.800$ M; (b) $[\mathrm{Tl^{III}}]_{\mathrm{tot}} = 0.500$ M and $[\mathrm{CN^-}]_{\mathrm{tot}} = 1.50$ M.

CN^-/Tl^{3+} conditions (vide infra), can be obtained during a time interval of 2 days in the Tl_2O_3−MCN−H_2O system:

$$\mathrm{Tl_2O_3(s) + 8CN^-(aq) + 3H_2O(l) \rightleftharpoons 2[Tl(CN)_4]^- + 6OH^-(aq)} \quad (7)$$

Increase of the molar ratio CN^-/Tl_2O_3 results in higher concentration of the tetracyano species.

II. Complex Formation in $\mathbf{Tl^{III}}$−$\mathbf{CN^-}$ Solutions. 1. Aqueous Solution. As it is mentioned above, thallium(III) forms $[\mathrm{Tl(CN)}_n(\mathrm{aq})]^{3-n}$ ($n = 1-4$) species with cyanide ion in aqueous solution.[4] Complexes with $n = 2-4$ can be observed by ^{205}Tl NMR spectra when dissolving Tl_2O_3 in aqueous HCN (Figure S1, Supporting Information). The ^{205}Tl chemical shifts are 2422, 2843, and 2989 ppm for the species with $n = 2$, 3, and 4, respectively. Because of high concentration of the $[\mathrm{Tl(CN)_3(aq)}]$ complex (∼0.15 M), the spin−spin coupling constant, ^{205}Tl−^{13}C ($^1J = 7.86$ kHz), can easily be seen in the spectra of the samples with naturally abundant carbon-13 content. Both chemical shifts ($\delta_{205\mathrm{Tl}}$, $\delta_{13\mathrm{C}}$) and spin−spin coupling constants ($^1J(^{205}\mathrm{Tl}-^{13}\mathrm{C})$) for the thallium(III)−cyano complexes obtained from the Tl_2O_3−HCN−H_2O systems are fully compatible with our previous data.[4]

The distribution of species in the solutions is in good agreement with the values calculated from the stability constants of the $[\mathrm{Tl(CN)}_n(\mathrm{aq})]^{3-n}$ ($n = 1-4$) complexes for the certain concentrations and pH (Figure 3a). The $[\mathrm{Tl(CN)_3(aq)}]$ complex dominates in all the solutions under these conditions (pH range 2.5−3.2, $[\mathrm{Tl^{III}}]_{\mathrm{tot}} = 80-800$ mM, $[\mathrm{CN^-}]_{\mathrm{tot}}/[\mathrm{Tl^{III}}]_{\mathrm{tot}} \approx 4-4.5$).[24] The fraction diagram shown in Figure 3a predicts that increasing of pH should shift the equilibrium between thallium(III)−cyano complexes to the $[\mathrm{Tl(CN)_4}]^-$ species. The pH of the solutions of thallium(III)−cyano species obtained from the Tl_2O_3−HCN−H_2O system increases slowly with time as a result of continuous redox reactions (vide infra) resulting in increase of the concentration of the tetracyano species (cf. Figure 4b).

Dissolution of Tl_2O_3 in aqueous solutions of alkali-metal cyanides leads to very basic (pH = 11.4−11.9) solutions; therefore, the equilibrium in the system is completely shifted to the $[\mathrm{Tl(CN)_4}]^-$ species.

II.2. Ether Solution. The $[\mathrm{Tl(CN)_3(aq)}]$ complex can be also obtained as the dominating species in aqueous solution at $CN^-/Tl^{3+} = 3$ (solution C) and suitable pH (Figure 3b). The complex cannot be nevertheless exclusively prepared in aqueous solution because of the equilibrium which also involves the $[\mathrm{Tl(CN)_2(aq)}]^+$ and $[\mathrm{Tl(CN)_4}]^-$ species (Figure 3b). However, we have found that mixing the Tl^{3+}−CN^-−H_2O solution ($CN^-/Tl^{3+} = 3$ and pH = 4.95) with diethyl ether results in a selective extraction of the triscyano−thallium(III) complex into the organic phase. No other thallium species could be detected by ^{205}Tl and ^{13}C NMR (cf. Figure S2, Supporting Information) in the ether solution (solution D) after phase separation. The chemical shifts and the coupling constant of the $Tl(CN)_3$ complex in water are found to be $\delta_{\mathrm{aq}}(^{13}\mathrm{C}) = 147.4$ ppm, $\delta_{\mathrm{aq}}(^{205}\mathrm{Tl}) = 2848$ ppm, and $^1J_{\mathrm{aq}}(^{205}\mathrm{Tl}-^{13}\mathrm{C}) = 7.95$ kHz.[4] The values of the chemical shifts and the coupling constant of the triscyano species are slightly different in ether solution, $\delta(^{13}\mathrm{C}) = 140.4$ ppm, $\delta(^{205}\mathrm{Tl}) = 2837$ ppm, and $^1J(^{205}\mathrm{Tl}-^{13}\mathrm{C}) = 7.54$ kHz, compared to the aqueous solution (vide supra and ref 4). Drying the water-saturated ether solution by dehydrating agents results in a decrease of the $Tl(CN)_3$ concentration. However, this does not effect the speciation, and the only detectable species is still the triscyano complex.

III. Redox Reactions in the $\mathbf{Tl_2O_3}$−HCN−$\mathbf{H_2O}$ System. 1. Reduction of $\mathbf{Tl^{III}}$ to $\mathbf{Tl^{I}}$. As it is mentioned above, apart from formation of the thallium(III)−cyano complexes, $[\mathrm{Tl(CN)}_n(\mathrm{aq})]^{3-n}$ ($n = 2-4$), an unavoidable partial reduction of thallium(III) to thallium(I) takes place when dissolving Tl_2O_3 in aqueous solutions of hydrogen cyanide. Efficiency of the reduction is dependent on a number of factors, including the concentration and the HCN/Tl_2O_3 ratio. Thus, over 10% of Tl^I (of total $[\mathrm{Tl}]_{\mathrm{tot}} = 0.8$ M) can be found in

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(24) Taking into account partial dissolution of thallium(III) oxide, the apparent $[\mathrm{CN^-}]_{\mathrm{tot}}/[\mathrm{Tl^{III}}]_{\mathrm{tot}}$ ratio in solution is higher than 3 in the case of HCN/Tl_2O_3 = 6 and substantially higher than 4 in the case of HCN/Tl_2O_3 = 8.

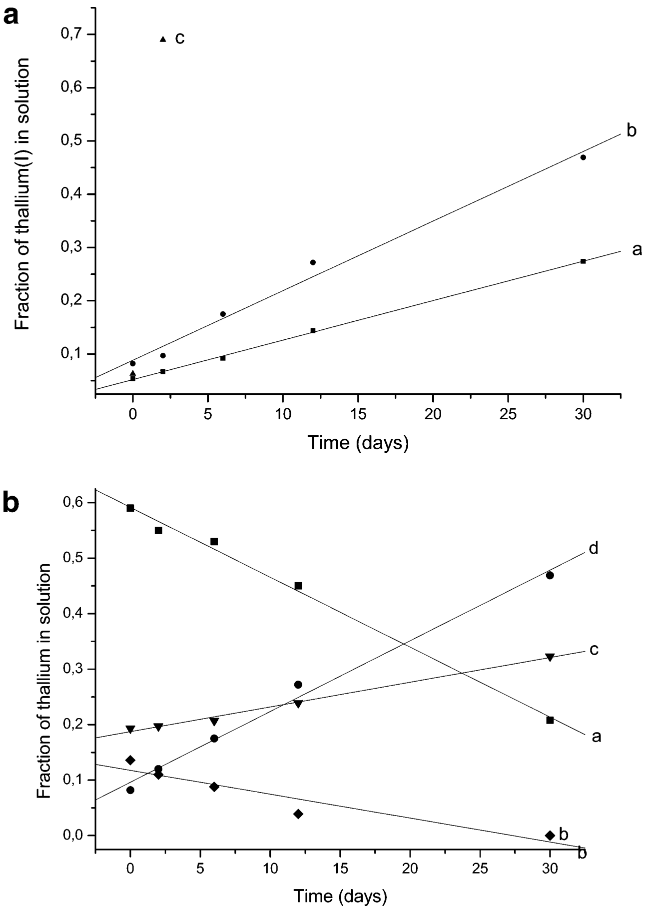

Figure 4. Part a shows the time dependence of the fraction of thallous ion in solutions obtained from the Tl_2O_3−HCN−H_2O system (HCN/Tl_2O_3 = 6; [HCN] = 0.31 M (a), 0.93 M (b and c)). $[Tl]_{tot}$ = 50 mM (a) and 200 mM (b and c). (a and b) The solutions were obtained by vigorous stirring of the heterogeneous mixtures during 8 h followed by filtration of the undissolved oxide. (c) An excess of Tl_2O_3 was added afterward to solution b and the mixture was stirred during 2 days followed by filtration of the oxide. Symbols are as follows: a, squares; b, filled circles; c, triangles. Part b shows the time dependence of the fraction of thallium species in solution obtained from the Tl_2O_3–HCN−H_2O system (HCN/Tl_2O_3 = 6; [HCN] = 0.93 M; $[Tl]_{tot}$ = 200 mM. Thallium species are as follows: $Tl(CN)_3(aq)$ (a); $Tl(CN)_2^+(aq)$ (c); $Tl(CN)_4^-$ (b); $Tl^+(aq)$ (d).

solution already after 1 h of stirring of the Tl_2O_3−HCN−H_2O mixture (5 M HCN) with the ratio HCN/Tl_2O_3 = 9.0 (pH = 2.71). Such a notable Tl^{III}/Tl^I reduction should be clearly attributed to reductive dissolution of the oxide by hydrogen cyanide as a reductant (cf. Figure 1a and reactions 3 and 5) taking place in the system along with acidic (enhanced by complex formation) dissolution (vide supra).

Although it has not been studied specially, it seems that the partial Tl^{III}/Tl^I reduction always accompanies reactions of the thallium(III) oxide in aqueous solution with reagents having low standard reduction potentials. Thus very effective redox reactions take place in the Tl_2O_3−H_nL−H_2O systems (H_nL = H_4EDTA,[25a] H_3NTA[25b]) resulting in partial decarboxylation of aminopolycarboxylic acids and formation of thallous ion along with the stable complexes of thallium(III) with complexones. At the same time, no reduction of thallium occurs when the aminopolycarboxylic ligands react with the $Tl^{3+}(aq)$ ion in acidic aqueous solutions of either $Tl(ClO_4)_3$ (in $HClO_4$)[8] or $Tl(NO_3)_3$ (in HNO_3).[26]

Reduction of thallium(III) inevitably takes place in solutions even after termination of the reaction between Tl_2O_3 and HCN. Figure 4a shows continuous increase of the Tl^I fraction in the solutions of $[Tl(CN)_n(aq)]^{3-n}$ complexes obtained from the Tl_2O_3−HCN−H_2O systems. Such an intense Tl^{III}/Tl^I reduction differs from the behavior of previously studied $Tl^{3+}(aq)$−H^+−CN^-−H_2O systems exhibiting substantially lower concentrations of the thallous ion even after longer time intervals.[4] Three distinctive features of the Tl_2O_3−HCN−H_2O system can be considered:

(i) The first feature is concentration. In most cases the $[Tl]_{tot}$ was substantially higher than in the previous work ($[Tl]_{tot} \leq 50$ mM [4]). As one can see from Figure 4a, reduction of the thallium(III) complexes proceeds significantly more quickly with increase of the concentration (cf. experimental points a and b).

(ii) The second feature is the molar ratio of HCN/Tl_2O_3. It has been noted[4] that increase of the CN^-/Tl^{3+} ratio (in acidic solution) results in significant intensification of the Tl^{III}/Tl^I reduction. When dissolving thallium(III) oxide in aqueous hydrogen cyanide, unavoidably a very large excess of HCN over Tl^{3+} is present in the solution at the beginning of the reaction, which can facilitate the reduction. It is also clear from Figure 1a that an increase of the HCN/Tl_2O_3 ratio, or the amount of the reductant, should facilitate formation of the thallous ion.

(iii) The third feature is thallium(III) oxide. The oxide itself seems to have an important role in the reduction. Incomparably higher rates of reduction can be reached by adding extra amounts of the Tl_2O_3 powder to the solutions containing the $[Tl(CN)_3(aq)]$ complex as the dominating species. Figure 4a demonstrates a drastic change which takes place in the solution of 200 mM $[Tl]_{tot}$ after stirring with added excess of Tl_2O_3 powder at room temperature (cf. experimental points b and c). After 2 days, almost 70% of thallium(III) in the solution has been reduced (Figure 4a (experimental point c)). The total thallium concentration in the solution barely changed indicating no net consumption of Tl_2O_3. Thallium(III) oxide has therefore itself a notable catalytic effect on the redox decomposition of the $[Tl(CN)_3(aq)]$ species. The pH of the solution increased from 2.7 to 7.5 after stirring, and the only thallium(III) species present in solution has been $[Tl(CN)_4]^-$.

Increase of temperature has also a profound effect on the redox reactions in the Tl_2O_3−HCN−H_2O system. Thus over 55% of Tl^I (of total $[Tl]_{tot}$ = 0.50 M) is found in solution after 7 days of continuous stirring of the Tl_2O_3−HCN−H_2O suspension (2 M HCN) with the ratio HCN/Tl_2O_3 = 6.0 at 70 °C.

III.2. Products of Oxidation of the Cyanide Ion. The redox reaction between thallium(III) oxide and hydrogen cyanide is expected to give cyanogen as a product of oxidation of HCN (cf. reaction 5). It has been shown that

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(25) (a) Tóth, I. Unpublished data. (b) Malyarik, M. A.; Ilyukhin, A. B. *Russ. J. Inorg.Chem.* **1998**, *43*, 865−874.

(26) Musso, S.; Anderegg, G.; Ruegger, H.; Schlapfer, C. W.; Gramlich, V. *Inorg. Chem.* **1995**, *34*, 3329−3338.

Table 2. ^{14}N NMR Chemical Shifts of Selected Nitrogen-Containing Species in Solution

species	δ (ppm)	reference
NH_4NO_3 (5 M in 2 M HNO_3)	-4.6 (NO_3^-) -351 (NH_4^+)	this work
HCN (in H_2O)	-129	this work
KCN (in H_2O)	-102	this work
KCN (8.5 M in H_2O)	-102.5	15b
KNCO (in H_2O)	-299	this work
KNCO (6.2 M in H_2O)	-302.9	15b
$(CONH_2)_2$ (DMSO-d_6)	-265	37

cyanogen is hydrolyzed by water in a set of competitive reactions:[2]

$$(CN)_2 + 4H_2O \rightleftharpoons (COO)_2^{2-} + 2NH_4^+ \qquad (8a)$$

$$(CN)_2 + 2H_2O \rightleftharpoons (CONH_2)_2 \qquad (8b)$$

$$(CN)_2 + 2H_2O \rightleftharpoons HCN + NH_3 + CO_2 \qquad (8c)$$

$$(CN)_2 + H_2O \rightleftharpoons HCN + HNCO \qquad (8d)$$

Products of oxidation of HCN/CN^- in the $Tl_2O_3-HCN-H_2O$ system have been studied by ^{14}N NMR. A typical ^{14}N NMR spectrum of the solution obtained from the system shows up to four signals significantly differing both in intensity and in line width (cf. Figure S3, Supporting Information). According to ^{205}Tl NMR, the sample contains the $[Tl^{III}(CN)_n(aq)]^{3-n}$ complexes ($n = 2-4$ with $n = 3$ being the dominating species) and Tl^I (10% of $[Tl]_{tot}$). A very broad (~1500 Hz) signal at ~ -90 ppm in the ^{14}N NMR spectrum is assigned to the ^{14}N resonances of the cyanide in the thallium(III)−cyano species and HCN (Table 2) occurring in fast chemical exchange at the current NMR time scale. The three other signals observed in the spectrum at ~ -270, -299, and -355 ppm are attributed to oxamide, cyanate, and ammonium ions, respectively (cf. Table 2), these being the products of hydrolysis of cyanogen in the solution.

Formation of oxamide and oxalate in the system (cf. reactions 8a and 8b) has also directly been confirmed by precipitation and X-ray analysis of low-soluble solids $(CONH_2)_2$ and $Tl^I_2C_2O_4$, respectively. Although the gas phase over the reaction mixture has not been analyzed, the species detected in aqueous solution and found in the solid state clearly indicate that the product of oxidation of hydrogen cyanide in the system is indeed cyanogen, $N{\equiv}C-C{\equiv}N$ (cf. reactions 8a,b).

One can suppose that it is reaction 8c that is responsible for the steady growing of the pH of the solutions (vide supra) since it gives rise to formation of ammonia ($K_b = 1.8 \times 10^{-5}$). Increase of pH brings in turn the equilibrium between the thallium(III)−cyano complexes toward the $[Tl(CN)_4]^-$ species. Thus, the two thallium species found in the solutions obtained from the $Tl_2O_3-HCN-H_2O$ system after longer storage or with redox reactions "catalyzed" by the excess of thallium(III) oxide are the thallous ion and the tetracyano complex of thallium(III).

IV. Crystal Structures. $Tl(CN)_3{\cdot}H_2O$ (1). Crystals of the compound have been obtained from water-saturated solutions of $Tl(CN)_3$ in diethyl ether (solution D). The $Tl(CN)_3{\cdot}H_2O$ crystals are unstable and decompose rapidly in air at room temperature forming brown Tl_2O_3. Drying the solution with dehydrating agents ($MgSO_4$ or P_2O_5) results in a continuous decrease of the concentration of the complex. As it can be expected, no $Tl(CN)_3{\cdot}H_2O$ crystals are obtained from the dehydrated solutions when evaporating the solvent. Similar to the Tl_2O_3-HCN system, a redox reaction between Tl^{III} and CN^- takes place yielding a low-soluble $Tl^I[Tl^{III}(CN)_4]$ compound (vide infra):

$$[Tl(CN)_3(aq)] \rightleftharpoons \{Tl(CN)_3\} + H_2O \qquad (9a)$$

$$2\{Tl(CN)_3\} \rightleftharpoons Tl[Tl(CN)_4](s) + (CN)_2 \qquad (9b)$$

The geometry of the thallium coordination environment in the structure of $Tl(CN)_3{\cdot}H_2O$ can be described as a distorted trigonal bipyramid (Figure 5a). The carbon atoms of the cyanide ligands are located in the equatorial plane of the polyhedron ($\angle C1-Tl1-C1 = 131.32(16)°$ and $\angle C1-Tl1-C2 = 114.22(12)°$). One axial position in the polyhedron is occupied by an oxygen atom of the water molecule, while the other is filled by a nitrogen atom from a cyanide ligand attached to the neighboring thallium complex (Figure 5b). The bridging mode of cyano groups in the structure, between equatorial (C-atom) and axial (N-atom) positions in the trigonal bipyramidal coordination, requires that the thallium polyhedra are twisted 90° relative to each other forming an infinite zigzag structure (Figure 5b). Addison angular structural parameter (an index of trigonality), τ, for the polyhedron is 0.67 and 0.73 when defining oxygen and nitrogen atoms, respectively, as the axial ligand in the square-pyramidal geometry.[27]

High instability of the $Tl(CN)_3{\cdot}H_2O$ crystals can be attributed to weakness of the Tl−O and Tl−N bonds. Water is very loosely coordinated to the thallium(III) ion in the $Tl(CN)_3{\cdot}H_2O$ compound, compare Tl−O distances in, for example, $[Tl(H_2O)_6]^{3+}$ in solid state, 2.23 Å ($[Tl(H_2O)_6](ClO_4)_3$),[7b] and in acidic aqueous solution, 2.21 Å,[7a] with 2.41 Å in the structure **1** (Table 3). Thallium(III)−nitrogen coordination in the compound should rather be attributed to completion of the metal's coordination sphere and/or crystal packing effects than to covalent bonding. The interatomic Tl−N distance in the compound (2.51 Å) is much longer than the "normal" $Tl^{III}-N$ bond length, compare with the value in, for example, $[Tl(NH_3)_6]^{3+}$ in liquid ammonia solution, 2.29 Å.[28] Similarly, a drastic difference in Tl−N bond length is observed in the polymer structure of a $[Tl(en)_2(CN)]_n(ClO_4)_{2n}$ compound, where a pseudooctahedral coordination of the thallium is built up by four nitrogen atoms of two bidentate-bound ethylenediamine ligands, a carbon atom of a cyanide ion, and a nitrogen atom from a cyanide coordinated to the neighboring thallium unit.[8c] The bond distances $Tl-N(-NH_2)$ (~2.31 Å) are much shorter than $Tl-N(-N{\equiv}C)$ (~2.57 Å).

The crystal structure of the $Tl(CN)_3{\cdot}H_2O$ compound supports our assumptions made previously for the thallium

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(27) Addison, A. W.; Nageswara Rao, T.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349−1356.

(28) Nilsson, K.; Persson, I. To be published.

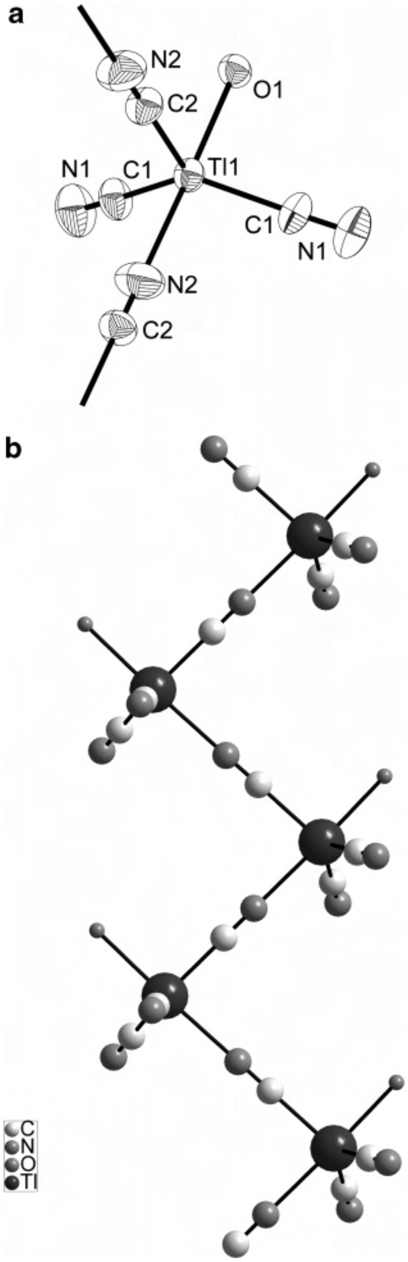

Figure 5. The structure of $Tl(CN)_3{\cdot}H_2O$ (compound **1**): (a) a fragment of the structure (ellipsoids at 50% probability level); (b) the extended structure.

coordination in the $Tl(CN)_3$ complex in aqueous solution. On the basis of the interatomic distances obtained from the EXAFS study, a structure with only one water molecule coordinated weakly to the thallium ion in the species, making up a distorted pseudotetrahedral polyhedron, has been proposed.[7a] The mean Tl−C bond length in the solid (∼2.15 Å) is the same as the Tl−C distance found for the complex in aqueous solution, while the Tl−O distance is slightly shorter, 2.41 and 2.42 Å, respectively. Similarity in the bond lengths in two polyhedra implies high flexibility of the triscyano complex. The configuration change can be visualized as a flip of the cyanides out of the trigonal plane caused by the scission of the Tl−N bond when dissolving the crystal in water, yielding the pseudotetrahedral geometry of the complex in aqueous solution.

$$[Tl(CN)_3(OH_2)(\mu\text{-NC})]_n(s) \rightleftharpoons [Tl(CN)_3(OH_2)](aq) \qquad (10)$$

$Tl^I[Tl^{III}(CN)_4]$ (2) and $K[Tl(CN)_4]$ (3). The compounds $Tl^I[Tl^{III}(CN)_4]$ and $K[Tl(CN)_4]$ are isostructural (Table 1). The structure is a derivative of Scheelite-type structures, $Ca[WO_4]$,[29a] in which, for example, $Tl^I[Tl^{III}Cl_4]$ is crystallized as well.[29b] The Scheelite's structural type allows widely different compositions of the compounds. Thus, substitution of the Tl^{3+} ion (0.89 Å) by the small B^{3+} (0.25 Å) ion[30] results in an isostructural compound $K[B(CN)_4]$.[29c] When oxygen (or chloride) atoms in the Scheelite's type structure are replaced by cyano groups, the ratio between the unit cell sides, c/a, decreases: 2.17, 2.23, 2.04, and 1.99 for $Ca[WO_4]$, $Tl^I[Tl^{III}Cl_4]$, $K[B(CN)_4]$, and $K[Tl(CN)_4]$, respectively. The c/a ratio for $Tl^I[Tl^{III}(CN)_4]$ is 2.

The crystal data for **2** (see Table 1 and Experimental Section) differ markedly from the data for the compound of the same composition, $Tl_2C_4N_4$, and formula, $Tl^I[Tl^{III}(CN)_4]$, reported by Williams et al.[10] The X-ray diffraction pattern of the latter structure was indexed by using primitive cubic cell with $a = 6.660$ Å. The chemical properties of this compound are also very different. Thus, in contrast to **2**, which is obtained from aqueous solution and is rather stable in air, it interacts readily with air and moisture. This implies that two distinct crystal phases, dependent on preparation method ("aqueous" or "water-free"), are available for the mixed valence $Tl^I[Tl^{III}(CN)_4]$ compound.

In the crystal structures **2** and **3**, thallium(III) has a nearly tetrahedral environment of carbons atoms, while nitrogen atoms occupy practically ideal cubic positions in the polyhedra of thallous and potassium ions, respectively (Figure 6). The Tl−C bond length in **3** (Table 3) is very similar (taking into account the larger uncertainty in interatomic distances determined by EXAFS) to the Tl−C distance found for the $[Tl^{III}(CN)_4]^-$ complex in aqueous solution (2.19(2) Å).[7a]

Mixed valence Tl^I-Tl^{III} compounds are very common in thallium chemistry. Depending on the Tl_mX_n stoichiometry, it is convenient to divide these compounds into several groups: Tl_4X_3 ($Tl^I_3[Tl^{III}X_3]$, $X = S^{2-}$ [31]), TlX ($Tl^I[Tl^{III}X_2]$, $X = S^{2-}$, Se^{2-},[31] CrO_4^{2-},[32] $N(CH_2COO)^{3-}$ [25b]), Tl_2X_3 ($Tl^I_3[Tl^{III}X_6]$ $X = Cl^-$,[33a] Br^- [33b]), and TlX_2 ($Tl^I[Tl^{III}X_4]$, $X = Cl^-$,[29b] Br^-,[34] CH_3COO^-, CN^-, N_3^- [3a]). Many of these mixed valence compounds have been prepared by reaction between thallium(III) oxide and an appropriate HX acid in an aqueous solution followed by precipitation of usually low-soluble thallous salts. The origin of appearance of thallium(I) ions in the systems was not specially discussed. However,

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Table 3. Selected Bond Lengths (Å) in Compounds **1**, **3**, **4**, and **5**

$Tl(CN)_3 \cdot H_2O^a$ (**1**)		$K[Tl(CN)_4]^b$ (**3**)		$Na[Tl(CN)_4] \cdot 3H_2O^c$ (**4**)		$Tl^I_2C_2O_4^d$ (**5**)	
C1−Tl#1	2.111(4)	Tl1−C1 (×4)	2.175(10)	Tl1−C1	2.178(8)	Tl1−O2#1	2.747(7)
N2−Tl1	2.508(6)	K1−N1 (×4)	2.958(12)	Tl1−C2	2.189(10)	Tl1−O2#2	2.752(8)
C2−Tl#2	2.189(7)	K1−N1#1 (×4)	3.305(14)	Tl1−C3	2.170(8)	Tl1−O2#3	2.859(8)
N1−C1	1.130(6)	N1−C1	1.153(14)	Tl1−C4	2.190(9)	Tl1−O1	2.766(8)
C2−N2	1.111(9)			Na1−O1	2.380(7)	Tl1−O1#1	2.950(8)
O1−Tl1	2.408(5)			Na1−O2	2.400(8)	Tl1−O1#4	3.088(9)
				Na1−O3	2.381(8)	Tl1−O1#5	3.090(8)
				Na1−N4	2.468(9)	O1−C1	1.26(3)
				Na1−N1#1	2.742(9)	O2−C1	1.28(2)
				Na1−N3#2	2.784(11)	C1−C1#2	1.50(4)
				N1−C1	1.133(11)		
				N2−C2	1.129(11)		
				N3−C3	1.129(12)		
				N4−C4	1.100(12)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) 1 − *x*, *y*, *z*; (#2) 1 − *x*, −0.5 + *y*, 0.5 − *z*; (#3) 1 − *x*, 0.5 + *y*, 0.5 − *z*. [b] Symmetry transformations used to generate equivalent atoms: (#1) −*x* + 1, −*y* + 1, −*z*. [c] Symmetry transformations used to generate equivalent atoms: (#1) *x* + 1/2, *y* − 1/2, *z*; (#2) −*x* + 1, *y*, −*z* + 1/2. [d] Symmetry transformations used to generate equivalent atoms: (#1) *x*, −*y* − 1/2, *z* + 1/2; (#2) −*x* + 1, −*y*, −*z*; (#3) −*x* + 1, *y* + 1/2, −*z* + 1/2; (#4) −*x*, −*y*, −*z*; (#5) *x*, −*y* + 1/2, *z* + 1/2.

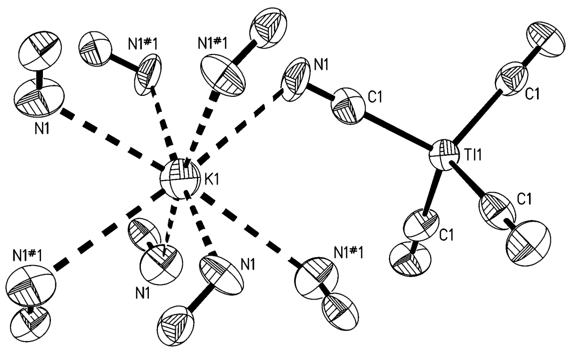

Figure 6. Fragment of the structure of $K[Tl(CN)_4]$ (compound **3**) (ellipsoids at 50% probability level).

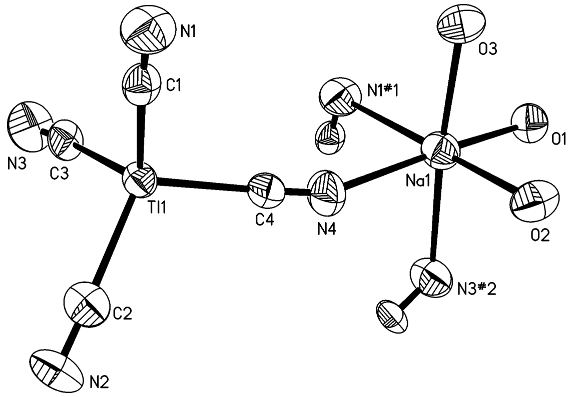

Figure 7. Fragment of the structure of $Na[Tl(CN)_4] \cdot 3H_2O$ (compound **4**) (ellipsoids at 50% probability level).

similarly to the Tl_2O_3−HCN−H_2O system, it can be attributed to a combined effect of reductive and acidic (enhanced by complex formation of Tl^{III}) dissolution of the oxide. The standard reduction potentials of the ligand X (X = S^{2-}, Se^{2-}, CH_3COO^-, $C_2O_4^{2-}$, CN^-, N_3^-) are low, and they can be readily oxidized by Tl^{III}. However, this redox reaction is not complete because of formation of stable complexes of thallium(III) with these ligands.

$Na[Tl(CN)_4] \cdot H_2O$ (4). The coordination environments of the sodium and thallium(III) ions in the crystal structure of $Na[Tl(CN)_4] \cdot 3H_2O$ are shown in Figure 7. In contrast to the thallous and potassium salts of the $[Tl(CN)_4]^-$ anion, the geometry of the sodium coordination in **4** is a pseudooctahedron. The *fac*-$[NaN_3O_3]$ polyhedron is built by nitrogen atoms of cyanide ions and water molecules. The thallium(III) coordination is similar to that in structures **2** and **3** and is formed by four carbon atoms of cyanide ligands. The mean Tl−C bond length in structure **4**, 2.18 Å (cf. Table 3), is very close to the value found in the structures of **2** and **3** (2.175 Å). It may be concluded that thallium(III) forms a very stable $[Tl(CN)_4]^-$ unit in the solid state, with the mean thallium−carbon distance barely influenced by the nature of the balancing cation. The interatomic distances Tl−C obtained for the tetracyano−thallium(III) complex in the solid state are slightly shorter than the values found for the $[Tl(CN)_4]^-$ species, 2.19(2) Å, in aqueous solution by LAXS technique.[7a]

$Tl_2^IC_2O_4$ (5). In structure **5**, the thallous ion has an irregular coordination geometry formed by seven oxygen atoms with Tl−O distances in the range 2.75−3.09 Å (Table 3) and a lone pair which clearly squeezes the Tl−O bonds in the polyhedron (Figure 8a). The sectors with thallium lone pairs are positioned in such a way to each other that it is possible to distinguish layers in the structure (Figure 8b). The only known thallium compound with oxalate is $Tl^IH_3(C_2O_4)_2 \cdot 2H_2O$.[35a] In that structure thallium is nine-coordinated by seven oxygen atoms of oxalate ions and two of water molecules. Isostructural dioxalates, $MH_3(C_2O_4)_2 \cdot 2H_2O$ (M = K^+,[35b] Rb,[35c] Cs^+,[35a] and NH_4^+ [35d]), have been prepared, whereas analogous oxalate salts, $M_2C_2O_4$, of the same cations have not been reported.

Conclusion

Thallium(III) oxide can be dissolved in water in presence of the strongly complexing cyanide ions. Tl^{III} is leached

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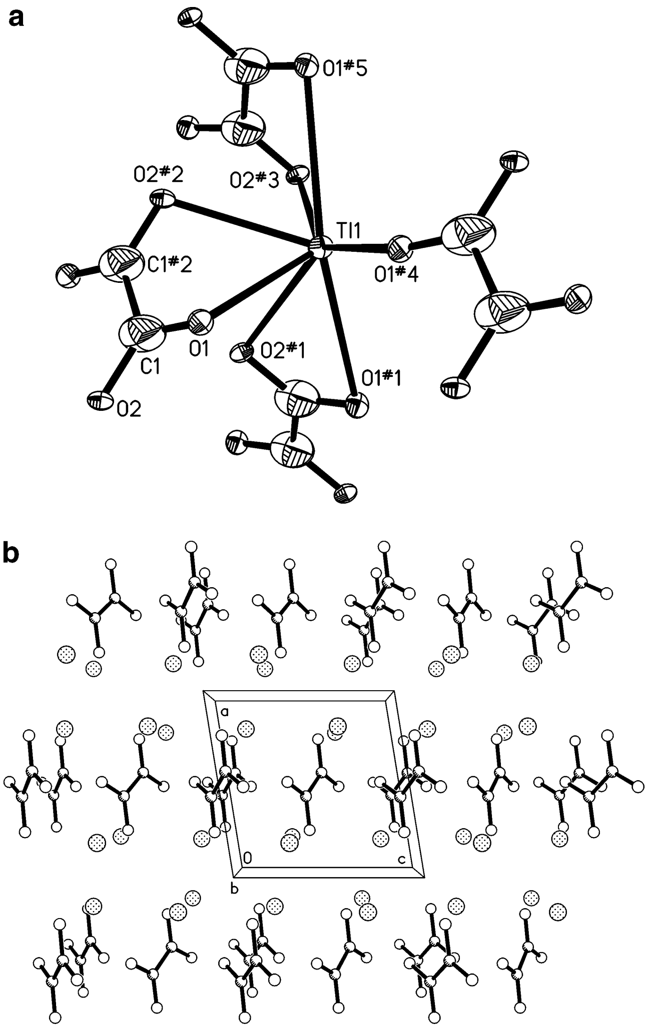

Figure 8. Fragment of the structure of $Tl^I_2C_2O_4$ (compound **5**) (ellipsoids at 50% probability level): (a) projection of the structure along the *b* axis; (b) the extended structure with thallium−oxygen contacts omitted for clarity.

from its oxide by both aqueous solutions of hydrogen cyanide and alkali-metals cyanides. The former method is more efficient, and up to 1 M concentration of thallium in solution can be obtained within a few hours. It has been demonstrated that the rate of dissolution is very much dependent on the HCN concentration and the HCN/Tl_2O_3 ratio. The dominating cyano complex of thallium(III) obtained in this way is $[Tl(CN)_3(aq)]$ which is present in equilibrium with bicyano and tetracyano species. When using aqueous solutions of the MCN (M = Na^+, K^+) salts to dissolve thallium(III) oxide, the equilibrium in the liquid phase is fully shifted to the $[Tl(CN)_4]^-$ complex dominating at higher pH and CN^-/Tl_2O_3 ratios.

The $Tl(CN)_3$ species can be selectively extracted from aqueous solution containing $CN^-/Tl^{III} = 3$ to diethyl ether. Depending on the water content in the ether phase, $Tl(CN)_3\cdot H_2O$ or $Tl^I[Tl^{III}(CN)_4]$ crystals can be prepared by slow evaporation of the solvent. In the crystal structure of $Tl(CN)_3\cdot H_2O$, the thallium(III) ion has a trigonal bipyramidal coordination with three cyanide ions in the equatorial plane, while an oxygen atom of the water molecule and a nitrogen atom from a cyanide ligand, attached to a neighboring thallium complex, form a linear O−Tl−N fragment. Cyanide ligands bridge the thallium units in an infinite zigzag chain structure.

Three compounds of the tetracyano−thallium(III) complex, $Na[Tl(CN)_4]\cdot 3H_2O$ and $M[Tl(CN)_4]$ (M = K^+, Tl^+), have been obtained, among which the $Tl^I[Tl^{III}(CN)_4]$ has been prepared by several methods. In the crystal structures of the $[Tl(CN)_4]^-$ the thallium ion has a distorted tetrahedral geometry with very similar mean Tl−C bond lengths.

Apart from the formation of the Tl^{III}−CN^- complexes, notable redox reactions occur in the Tl_2O_3−HCN−H_2O system. This indicates that along with the acidic leaching (enhanced by Tl^{III}−CN^- complex formation) an effective reductive dissolution of the thallium(III) oxide also takes place in the solutions containing readily oxidized hydrogen cyanide. The redox reaction is terminated when all thallium is present in the forms of Tl^I (product of reduction) and the most stable cyano complex of thallium(III), $[Tl(CN)_4]^-$. Hydrogen cyanide is oxidized by thallium(III) to cyanogen whose formation has indirectly been confirmed via products of its hydrolysis in water, that is, oxalate ion and oxamide, detected both in solution and in the solid phase. Other products of the hydrolysis of cyanogen include NH_4^+ and NCO^- ions. Three crystalline compounds, $Tl^I[Tl^{III}(CN)_4]$, $Tl^I_2C_2O_4$, and $(CONH_2)_2$, have been obtained as products of the redox reactions in the Tl_2O_3−HCN−H_2O system.

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Supporting Information Available: Table of observed and calculated *d* spacings and relative intensities in the X-ray diffraction powder pattern of compound $Tl^I[Tl^{III}(CN)_4]$, ^{205}Tl and ^{14}N NMR spectra of the solutions obtained from the Tl_2O_3−HCN−H_2O system, as well as ^{205}Tl and ^{13}C spectra of water saturated solutions of a $Tl(CN)_3$ complex in diethyl ether (pdf); X-ray crystallographic data (cif format). This material is available free of charge via the Internet at http://pubs.acs.org.

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