

# Equilibria and Dynamics of Tl(edta)X<sup>2-</sup> Complexes (X = Halide, Pseudohalide) Studied by Multinuclear NMR<sup>1</sup>

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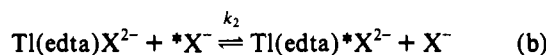
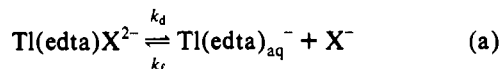
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Equilibria and dynamics in aqueous solutions of mixed complexes Tl(edta)X<sup>2-</sup> containing ionic medium (1 M NaClO<sub>4</sub>) have been studied by means of <sup>205</sup>Tl-, <sup>15</sup>N-, <sup>13</sup>C-, and <sup>1</sup>H-NMR and potentiometry. Individual <sup>205</sup>Tl chemical shifts have been determined for all the investigated complexes (X = H<sub>2</sub>O, OH, Cl, Br, CN, SCN). For the pseudohalide complexes the <sup>15</sup>N- and <sup>13</sup>C-NMR shifts as well as the spin-spin coupling constants  $J(^{205}\text{Tl}-^{15}\text{N})$  and  $J(^{205}\text{Tl}-^{13}\text{C})$  have also been determined. The coupling constant  $J(^{205}\text{Tl}-^{13}\text{C})$  for the complex Tl(edta)CN<sup>2-</sup> is remarkably large, 10 479 Hz, indicating a very strong thallium-carbon bond. The stability constants,  $K_X = [\text{Tl}(\text{edta})\text{X}^{2-}]/\{[\text{Tl}(\text{edta})^-][\text{X}^-]\}$ , determined by a combination of <sup>205</sup>Tl- and <sup>13</sup>C-NMR and potentiometry, for X = Cl, CN, and SCN are, respectively: log  $K_X = 2.6 (\pm 0.1 = \sigma)$ , 8.72 ( $\pm 0.03$ ) and 2.70 ( $\pm 0.03$ ). The kinetics for the X-ligand exchange was found to follow the rate equation

$$-d[\text{Tl}(\text{edta})\text{X}^{2-}]/dt = k_d[\text{Tl}(\text{edta})\text{X}^{2-}] + k_2[\text{Tl}(\text{edta})\text{X}^{2-}][\text{X}^-]$$

which can be ascribed to the reactions



where  $k_d$  is  $\geq 1.7 \times 10^4$ ,  $2.7 (\pm 0.1 = \sigma) \times 10^4$ ,  $< 3$ , and  $2.4 (\pm 0.1) \times 10^4 \text{ s}^{-1}$  for X = Cl, Br, CN, and SCN, respectively, and  $k_2$  is  $1.5 (\pm 0.1) \times 10^6$  and  $3.0 (\pm 0.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , for X = CN and SCN, respectively. In order to facilitate the discussion of reaction mechanisms, the crystal and molecular structure of the compound Na<sub>2</sub>[Tl(edta)CN]·3H<sub>2</sub>O has been determined using single-crystal X-ray diffraction. This compound crystallizes in the monoclinic space group *P*2<sub>1</sub>/*c* (no. 14) with  $a = 7.769 (2) \text{ \AA}$ ,  $b = 14.130 (6) \text{ \AA}$ ,  $c = 17.069 (5) \text{ \AA}$ ,  $\beta = 101.44 (2)^\circ$ , and  $Z = 4$ . Thallium is coordinated by edta (hexadentate coordination) and cyanide; i.e., no water molecule is present in the first coordination sphere of thallium. The thallium atom is about 0.08 Å below the distorted plane of the four coordinated edta oxygens. Taking into account that the values of the formation rate constants  $k_f^X$  for at least X = Br and SCN are close to each other, a mechanism involving dissociation of a water molecule from the Tl(edta)<sub>aq</sub><sup>-</sup> complex as a rate-determining step can be proposed for reaction type a. The rate constant for this step can be estimated to  $k_w \sim 1.3 \times 10^8 \text{ s}^{-1}$  (for dissociation of one particular water molecule). A similar rate-determining step can be proposed for reaction b. In this case  $k_w \sim 1.9 \cdot 10^8 \text{ s}^{-1}$ , close to the one for reaction a and slightly higher than the corresponding value ( $5 \times 10^7 \text{ s}^{-1}$ ) for the aquated Tl<sup>3+</sup> ion, in agreement with the expected influence of the decrease of the coordination number of thallium(III) from Tl(edta)<sub>aq</sub><sup>-</sup> to Tl<sub>aq</sub><sup>3+</sup>.

## Introduction

Metal-polydentate ligand complexes play an essential role in the migration of metal ions in natural waters<sup>3</sup> and are also important for the routes of metal-containing species in biological systems.<sup>4</sup> Most of the studies of these complexes have been performed on transition metals, whereas the literature on the main group metals is relatively limited. For group 13 of the periodic table some equilibrium information is available for complexes of aluminium(III), gallium(III), indium(III), and thallium(III).<sup>5,6</sup>

Thallium(III) ethylenediaminetetraacetate, Tl(edta)<sup>-</sup>, is one of the most stable metal-edta, M(edta), complexes, with log  $K = 37.8$ ;<sup>5</sup> only Co<sup>III</sup>(edta)<sup>-</sup> is more stable. Metal ions in M(edta) complexes are not always coordinatively saturated, because of the large size and coordination number >6 of the metal ion and/or because of the decreased denticity of the ligand, edta.<sup>7</sup> In fact, Tl(edta)<sup>-</sup> forms quite stable mixed ligand complexes, Tl(edta)X<sup>2-</sup> (X = Cl, Br, I).<sup>8</sup>

Information about dynamics of aluminium group elements in solution is more scarce. Solvent exchange mechanisms for Al,

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Ga, and In have been studied by research groups of van Eldik,<sup>9</sup> Merbach,<sup>10</sup> and Tanaka.<sup>11</sup> Our knowledge about dynamic properties of thallium(III) in solution is even more limited. For solvent exchange, there are only two recent papers dealing with water exchange rate for hydrated Tl(III) ion.<sup>12,13</sup>

Recently, we have established the formation and redox stability of cyanothallium(III) complexes<sup>14</sup> and of the species Tl(SCN)<sup>2+</sup> in aqueous solution.<sup>15</sup> Continuing our work on the chemistry of Tl(III) we here report a study of equilibria and dynamics of Tl(edta)<sup>-</sup>X<sup>-</sup> systems (where X<sup>-</sup> = CN<sup>-</sup>, SCN<sup>-</sup>, Cl<sup>-</sup> and Br<sup>-</sup>) in aqueous solution using <sup>205</sup>Tl-, <sup>13</sup>C-, <sup>15</sup>N-, and <sup>1</sup>H-NMR and potentiometry. In order to support our mechanistic considerations, we have also determined the solid-state structure of Na<sub>2</sub>Tl(edta)CN·3H<sub>2</sub>O by single crystal X-ray diffraction.

## Experimental Section

**Materials and Preparation of Solutions.** The stock solution of concentrated acidic Tl(ClO<sub>4</sub>)<sub>3</sub> was prepared by anodic oxidation of TlClO<sub>4</sub>.<sup>16</sup> A stock solution of NaTl(edta) was obtained by adding dropwise an equivalent quantity (15 mmol) of 0.1 M solution of Na<sub>2</sub>H<sub>2</sub>(edta) to a stirred solution of acidic 0.70 M Tl(ClO<sub>4</sub>)<sub>3</sub> (15 mmol). The solution of Na<sub>2</sub>H<sub>2</sub>(edta) contained a calculated quantity of NaOH in order to neutralize (a) HClO<sub>4</sub> in the Tl(ClO<sub>4</sub>)<sub>3</sub> stock solution and (b) the protons originating from Na<sub>2</sub>H<sub>2</sub>edta. pH was finally adjusted to 2.80, so that only the complex Tl(edta)<sup>-</sup> was present.<sup>5</sup> The pH adjustment (if needed) was done using relatively concentrated solutions of NaOH or HClO<sub>4</sub> in order to avoid noticeable dilution of the samples. The resulting solution was kept dark to avoid photochemical decomposition.<sup>17</sup> For NMR samples, a weighed quantity of solid sodium halide or pseudohalide salt was added to the known volume of the Tl(edta)<sup>-</sup> solution. The salts, NaClO<sub>4</sub>, NaCl, NaBr, NaSCN, and NaCN (Merck, analytical grade), were used without further purification. The ionic strength was kept approximately constant at I = 1 M (NaClO<sub>4</sub>).

Single crystals of Na<sub>2</sub>Tl(edta)CN·3H<sub>2</sub>O were grown at the interface between 96% ethanol and an aqueous solution containing a slight excess (1.05 equiv of CN per Tl) of solid NaCN in the NaTl(edta) stock solution.

For <sup>13</sup>C-NMR measurements, <sup>13</sup>C-enriched (75%) NaSCN was prepared from <sup>13</sup>C-enriched NaCN (99%, Cambridge Isotope Labs., Woburn, Mass., USA) as described earlier.<sup>15</sup> For <sup>15</sup>N-NMR, <sup>15</sup>N-enriched NaCN and NaSCN (99%) were purchased from MSD Isotopes, Montreal, Canada. <sup>1</sup>H-NMR measurements were performed on solutions containing ~99% D<sub>2</sub>O as solvent.

**Analysis.** The analysis of Tl(III), Tl<sup>+</sup>, and H<sup>+</sup> in the Tl(ClO<sub>4</sub>)<sub>3</sub> stock solution was described earlier.<sup>14</sup> The content of Tl(I) and (after reduction with SO<sub>2</sub>) of Tl(III) in the NaTl(edta) stock solution was determined by titration with KBrO<sub>3</sub>, in about 5 M HCl. The presence of edta did not disturb the titration. No reduction of Tl(III) occurred during the preparation of NaTl(edta) solution. The <sup>13</sup>C-enriched NaSCN was checked by recording <sup>13</sup>C-NMR spectra of an aqueous solution of this salt; no cyanide signal was found. The thiocyanate content in NaSCN was analyzed by Volhard's method.<sup>18</sup>

**pH Measurements.** pH values were measured by a combination electrode (Radiometer GK2401 B) connected to a pH-meter (Radiometer PHM62 or PHM84). In order to remove potassium and thus to avoid precipitation of KClO<sub>4</sub> in the electrode membrane, the inner solution of the electrode (KCl in water) was replaced with 1 M NaCl saturated with

AgCl. The pH-meter was calibrated by Irving's method.<sup>19</sup> This calibration and the NMR measurements (peak integrals and time-averaged chemical shift values) lead to stoichiometric concentrations (i.e. not activities). Thus, throughout this paper we deal with so called "stoichiometric" (based on concentrations) equilibrium constants. pH values of the NMR samples were measured before the NMR measurement and controlled after it. The <sup>13</sup>C-NMR chemical shift of the signal for the free CN<sup>-</sup> is dependent on pH;<sup>20</sup> this independently measured δ<sub>C</sub> vs pH curve was also used to check the pH in dilute samples.

**NMR Measurements.** All NMR spectra were recorded with a Bruker AM400 spectrometer at a probe temperature of 25 (±0.5) °C, if not stated otherwise. NMR parameters were chosen in order to obtain quantitative spectra and hence peak integrals could be used for calculation of stability constants. Typical values are as follows.

<sup>205</sup>Tl-NMR: spectrometer frequency (SF) = 230.8 MHz; spectral window (SW) = 60–125 kHz; flip angle ~25° (15 μs); pulse repetition time ~0.1 s; digital resolution (DR) = 244 Hz/point; number of scans (NS) = 1000–5000. (The flip angle was shorter and the pulse repetition time was longer, up to 1 s for quantitative integrals). The chemical shift values are referred in ppm toward higher frequency from the <sup>205</sup>Tl-NMR signal of an aqueous solution of TlClO<sub>4</sub> extrapolated to infinite dilution. Since the chemical shifts of aqueous solutions of different Tl(I) salts extrapolate to the same value at infinite dilution,<sup>21</sup> this value corresponds to the chemical shift of the free hydrated Tl<sup>+</sup> ion. The accuracy of the measured integrals and line widths is estimated to be 10–15%; the chemical shift values are accurate to ±(0.5–2) ppm depending on the line width.

<sup>13</sup>C-NMR: SF = 100.6 MHz; SW = 17 kHz; flip angle ~10°; pulse repetition time = 0.3 s (1 s when quantitative integrals were needed); DR = 2.1 Hz/point; NS = 1000–10 000. Usually only the signals related to the <sup>13</sup>C-enriched CN<sup>-</sup> or SCN<sup>-</sup> were followed, in contrast to the small signals of the nonenriched edta ligand. The chemical shifts are reported in ppm toward higher frequency with respect to an external sample of the water-soluble sodium derivative of TMS.

<sup>15</sup>N-NMR: SF = 40.55 MHz; SW = 2 kHz, flip angle ~90°; pulse repetition time = 0.6 s; DR = 1.59 Hz/point; NS = 500. Chemical shifts are given in ppm toward higher frequency from an external solution of NaSC<sup>15</sup>N (0.032 M, 25 °C) at 0 ppm, corresponding to +202.4 ppm from neat NH<sub>3</sub> (25 °C).

<sup>1</sup>H-NMR: SF = 400.13 MHz; SW = 3200; flip angle ~70°; pulse repetition time = 6 s; DR = 0.2 Hz/point; NS = 40. Chemical shifts are given in ppm toward higher frequency from external TMS.

**X-ray Diffraction Study of Na<sub>2</sub>Tl(edta)CN·3H<sub>2</sub>O.** An irregular crystal, with approximate dimensions 0.12 × 0.15 × 0.25 mm, enclosed in a thin-walled glass capillary was used for the data collection. The data collection was performed on a Syntex P2<sub>1</sub> four-circle diffractometer using λ(Mo Kα) radiation with a graphite monochromator. The SHELXTL PLUS (PC Version) program package was used for all calculations.<sup>22</sup>

The crystals are monoclinic with the following unit cell parameters: a = 7.769 (2) Å, b = 14.130 (6) Å, c = 17.069 (5) Å, and β = 101.44 (2)°. D<sub>m</sub> = 2.25, g cm<sup>-3</sup>, D<sub>x</sub> = 2.237 g cm<sup>-3</sup>, Z = 4, μ = 8.90 mm<sup>-1</sup>, V = 1836.5 (9) Å<sup>3</sup>, and λ = 0.710 73 Å. The θ/2θ-scan technique with variable scan speed (from 2° min<sup>-1</sup> to 29.3° min<sup>-1</sup>) was used. Three check reflections were measured after every 100 reflections. Their intensities decreased gradually and were about 50% lower at the end of the data collection (after ~230 h). The data were corrected to compensate for this decomposition due to the exposure of the compound to the X-rays. A total of 5919 reflections were measured for 3° < 2θ < 60° (i.e. up to (sin θ/λ) = 0.70). Of these, 5339 reflections were independent, and 2644 reflections with intensities greater than 2σ(I) were used in the calculations. An empirical absorption correction, using six parameters to define a pseudoellipsoid, was applied to the data. The absorbance varied between 0.135 and 0.175. The centrosymmetric space group P2<sub>1</sub>/c (No. 14) was uniquely determined from the systematic extinctions.

The position of the thallium atom was determined from a three-dimensional Patterson map (R = 21.2%), and the positions of the remaining non-hydrogen atoms were found from successive Fourier difference syntheses. Least-squares refinement with isotropic temperature factors led to R = 10.4% for 113 refined parameters. Introduction of an anisotropic temperature factor for the Tl atom reduced the R value to

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**Table I.** Thermodynamic and NMR Data for the Complexes  $\text{Tl}(\text{edta})\text{X}^{2-}$  ( $\text{X} = \text{CN}, \text{SCN}, \text{Cl}, \text{Br}$ ) at 25 °C: Stability Constants ( $K_X = [\text{Tl}(\text{edta})\text{X}^{2-}]/[\text{Tl}(\text{edta})][\text{X}^-]$ ), Individual  $^{205}\text{Tl}$ -,  $^{13}\text{C}$ -, and  $^{15}\text{N}$ -NMR Chemical Shifts, Nonexchange Line Widths,  $\Delta\nu^\circ$ , and Spin-Spin Coupling Constants ( $J_{\text{Tl-X}}$ )

species	log $K_X$	$\delta(^{205}\text{Tl})$ (ppm)	$\Delta\nu^\circ(^{205}\text{Tl})$ (Hz)	$\delta(^{13}\text{C})$ (ppm)	$\Delta\nu^\circ(^{13}\text{C})$ (Hz)	$J(^{205}\text{Tl}-^{13}\text{C})$ (Hz)	$\delta(^{15}\text{N})$ (ppm)	$J(^{205}\text{Tl}-^{15}\text{N})$ (Hz)
$\text{Tl}(\text{edta})^-$		2301	1200					
$\text{Tl}(\text{edta})(\text{OH})^{2-}$	-6.00 <sup>a</sup>	2313	1200					
$\text{Tl}(\text{edta})\text{Cl}^{2-}$	2.30 <sup>b</sup>	2308	1300					
$\text{Tl}(\text{edta})\text{Br}^{2-}$	3.50 <sup>b</sup>	1883	1300					
$\text{Tl}(\text{edta})\text{CN}^{2-}$	8.72 ± 0.03	2460	1100	150.5	5	10 479 ± 30	68.0 <sup>e</sup>	11
$\text{Tl}(\text{edta})\text{SCN}^{2-}$	2.70 ± 0.03	2385	1200	121.6	5	386 ± 10 <sup>d</sup>	39.2 <sup>e</sup>	f
HCN	9.09 <sup>c</sup>			114.85	2 <sup>c</sup>			
$\text{CN}^-$				168.0	2 <sup>c</sup>			
$\text{SCN}^-$				136.2	5			

<sup>a</sup>  $K = [\text{Tl}(\text{edta})(\text{OH})^{2-}][\text{H}^+]/[\text{Tl}(\text{edta})^-]$ .<sup>5,8</sup> <sup>b</sup> Reference 8. <sup>c</sup> Reference 20. <sup>d</sup> Calculated (see text). <sup>e</sup> Referenced to an external aqueous solution of  $\text{NaSC}^{15}\text{N}$  (32 mM, 25 °C) at 0 ppm. <sup>f</sup> Not observed in the spectra.

9.5%. The highest remaining peaks (all lower than  $4 \text{ e } \text{\AA}^{-3}$ ) in the final difference Fourier map were positioned close to the Tl atom (and a few close to Na), indicating errors in the absorption correction and in the model of the thermal movement. Further refinements were not meaningful because of the deterioration of the crystal during the data collection (see above) which lowered the quality of the experimental data. The refinements were based on minimization of  $\sum w(|F_o| - |F_c|)^2$ , including reflections with  $|F_o| > 4\sigma(F_o)$ . The weighting function used was  $w = 1/[\sigma^2(F_o) + (0.03F_o)^2]$ .

## Results and Discussion

**NMR Parameters.** The obtained NMR parameters of mixed ligand complexes, i.e. the chemical shifts, line widths, and spin-spin coupling constants, are summarized in Table I. The  $^{205}\text{Tl}$ -NMR signal of  $\text{Tl}(\text{edta})^-$  appears at  $\delta_{\text{Tl}} = 2301$  ppm, about +215 ppm from  $\text{Tl}_{\text{aq}}^{3+}$ .<sup>14</sup> Although we have not been able to find chemical shift for any comparable thallium(III) compound, our value is in general agreement with the observed chemical shift of Tl(III) coordination compounds in solution.<sup>23a-c</sup> A recent paper<sup>23d</sup> gives  $\delta_{\text{Tl}} = 234$  and 354 ppm (from an aqueous saturated solution of  $\text{TlNO}_3$ ) for the compounds  $\text{Tl}(\text{NTA}-3\text{H})_2^{3-}$  and  $\text{Tl}(\text{DTPA}-5\text{H})^{2-}$ , respectively. These values are probably not reliable; no other signals of thallium(III) compounds have previously been found in this region.<sup>23a-c</sup> The line widths of the  $^{205}\text{Tl}$ -NMR signals are about 1200 Hz, substantially broader than the corresponding value of  $\sim 40$  Hz obtained for the  $\text{Tl}(\text{CN})_n^{3-n}$  complexes.<sup>14</sup> The broadening can be attributed to spin-spin coupling between  $^{205}\text{Tl}$  and the 12 (i.e. 4 + 8)  $^1\text{H}$  nuclei of the edta ligand.<sup>17</sup> The  $^1\text{H}$ -NMR spectrum of  $\text{Tl}(\text{edta})^-$  (cf. Supplementary Material) consists of peaks at  $\sim 2.45$  and 3.9 ppm ( $\delta_{\text{H}} = 3.168$  ppm) belonging to the doublet of the Tl-coupled central edta protons,  $^3J(\text{Tl}-^1\text{H}) = 293.86(2)$  Hz; the  $^1\text{H}$  signal of the acetate arms of the edta appears as an ABX pattern with  $\delta_{\text{H}}^{\text{A}} = 3.664$  ppm,  $\delta_{\text{H}}^{\text{B}} = 3.441$  ppm,  $^3J(^1\text{H}_{\text{A}} - ^1\text{H}_{\text{B}}) = -16.82(2)$  Hz,  $^3J(\text{Tl}-^1\text{H}_{\text{A}}) = 308.36(2)$  Hz, and  $^3J(\text{Tl}-^1\text{H}_{\text{B}}) = 361.68(2)$  Hz, as obtained from a simulation of the spin system.<sup>24</sup> These coupling constants cannot be seen in a  $^{205}\text{Tl}$ -NMR spectrum (especially at high magnetic field where the thallium signal is broadened by chemical shift anisotropy relaxation), and only a (nearly Lorentzian) broad band appears. Our attempts to record  $^{205}\text{Tl}$ -NMR proton-decoupled spectra were not successful. The effect of this "hidden" multiplet will be further discussed in the kinetic part of this paper. Still, the large chemical shift difference between  $\text{Tl}(\text{edta})^-$  and, e.g.,  $\text{Tl}(\text{edta})\text{CN}^{2-}$  (cf. Table I) made the integration of these broad signals possible. Formation of mixed

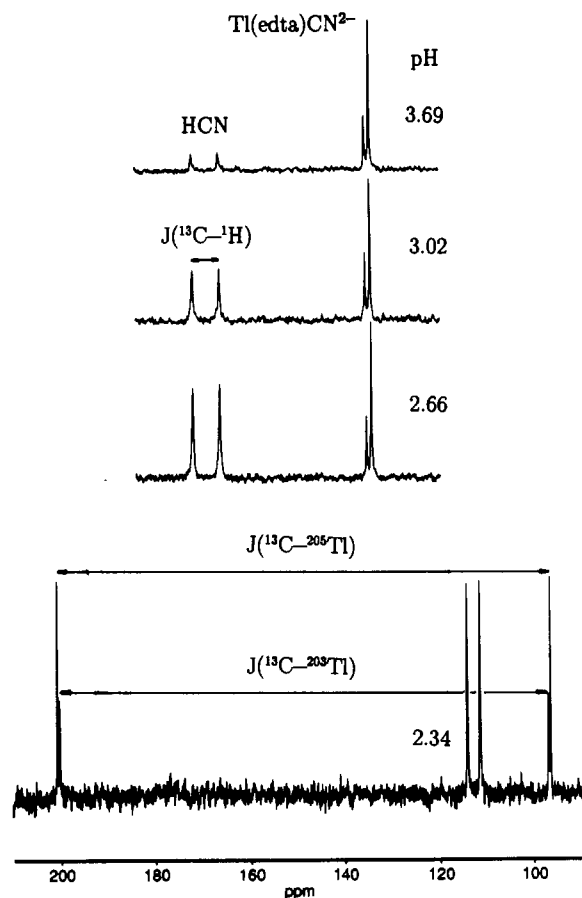
complexes,  $\text{Tl}(\text{edta})\text{X}^{2-}$ , leads to a higher  $^{205}\text{Tl}$ -NMR chemical shift than that of  $\text{Tl}(\text{edta})^-$  for all of the studied ligands X, except  $\text{Br}^-$ . The same trend of the chemical shifts was found for  $\text{TlX}^{2+}$  complexes as compared to the shift of  $\text{Tl}_{\text{aq}}^{3+}$ ,<sup>14,25</sup> but no obvious correlation could be found between the chemical shift values and other physicochemical properties of the complexes (e.g. stability constant, bond length, or "softness" of the ligand). The  $^{205}\text{Tl}$ -NMR chemical shift of  $\text{Tl}(\text{edta})(\text{OH})^{2-}$  differs only slightly from that for  $\text{Tl}(\text{edta})^-$  ( $\Delta\delta = \delta_{\text{Tl}(\text{edta})(\text{OH})^{2-}} - \delta_{\text{Tl}(\text{edta})^-} = 12.4$  ppm), which can be due to nearly the same structure and set of donor atoms in these complexes in solution. In the crystals of  $\text{CaTl}(\text{edta})(\text{OH})\cdot 3\text{H}_2\text{O}$ , thallium(III) is coordinated by six donor atoms of edta and by one  $\text{OH}^-$ , whereas the structure of the complex  $\text{Tl}(\text{edta})_{\text{aq}}^{+}$  has not been determined.<sup>26</sup> Formation of  $\text{Tl}(\text{edta})\text{Cl}^{2-}$  from  $\text{Tl}(\text{edta})^-$  has also a small effect on  $\delta_{\text{Tl}}$  ( $\Delta\delta = 8$  ppm), in contrast to  $\text{TlCl}^{2+}$  having  $\Delta\delta' = \delta_{\text{TlX}} - \delta_{\text{Tl}(3+)} = 198$  ppm.<sup>25</sup> The formation of the mixed complexes with more "soft" X ligands<sup>27</sup> has a much larger effect on the chemical shifts,  $\Delta\delta = +84.4$ ,  $-417.6$ , and  $+152.4$  ppm, compared to  $\Delta\delta'$  values of  $+204$ ,  $-548$ , and  $+224$  ppm for  $\text{X} = \text{SCN}^-$ ,<sup>15</sup>  $\text{Br}^-$ ,<sup>25</sup> and  $\text{CN}^-$ ,<sup>14</sup> respectively. The low-frequency shift of  $\text{Tl}(\text{edta})\text{Br}^{2-}$  ( $\Delta\delta = -417.6$  ppm) can be due to the "heavy atom shift".<sup>28</sup>

$^{13}\text{C}$ -NMR shifts for the  $\text{SCN}^-$  and  $\text{CN}^-$  signals are given in Table I. The  $^{13}\text{C}$ -NMR chemical shift of  $\text{Tl}(\text{edta})(\text{SCN})^{2-}$  is 121.6 ppm, which is less shifted from the position of the free  $\text{SCN}^-$ ,  $\delta_{\text{C}} = 136.2$  ppm, than is the signal of  $\text{Tl}(\text{SCN})^{2+}$  (114.15 ppm).<sup>15</sup> In both cases the chemical shifts are in the range for S-bonded  $\text{SCN}^-$  complexes.<sup>29</sup> The value of  $\delta_{\text{C}} = 150.5$  ppm for  $\text{Tl}(\text{edta})\text{CN}^{2-}$  is only slightly higher than the corresponding value for  $\text{Tl}(\text{CN})^{2+}$  (141.21 ppm),<sup>14</sup> and it is very close to the chemical shift values of diamagnetic tetrahedral tetracyano complex,  $\text{MX}_4^{2-}$  ( $\text{M} = \text{Zn}, \text{Cd}, \text{and Hg}$ ).<sup>30</sup> The formation of the mixed complexes affects slightly the chemical shifts and the  $^2J(^{205}\text{Tl}-^{13}\text{C})$  values of the coordinated edta entity as compared to  $\text{Tl}(\text{edta})^-$ ,<sup>17</sup> but these signals were used only in special cases (see Equilibrium Dynamics, Section I(a)).

The  $^{15}\text{N}$ -NMR chemical shift of  $\text{Tl}(\text{edta})(\text{SCN})^{2-}$  is +39.2 ppm from the shift of free  $\text{SCN}^-$ . This large positive shift indicates clearly the S-bonded character of the mixed complex,<sup>31</sup> in agreement with the  $^{13}\text{C}$ -NMR results (see above). The  $^{15}\text{N}$ -

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(31) Pregosin, P. S.; Streit, H.; Venanzi, L. M. *Inorg. Chim. Acta* **1980**, *38*, 237.



**Figure 1.** Tl(edta)<sup>-</sup>-CN<sup>-</sup> system. 100-MHz <sup>13</sup>C-NMR spectra of an aqueous solution containing 0.010 M Tl(edta)<sup>-</sup>, 0.010 M NaCN (enriched to 99% in <sup>13</sup>C), and 1 M NaClO<sub>4</sub> at different pH values and 25 °C. The inserted spectra show an expanded chemical shift region (90–120 ppm) to exhibit the spin–spin couplings  $J(^{13}\text{C}-^{205}\text{Tl})$  and  $J(^{13}\text{C}-^{203}\text{Tl})$  in the complex Tl(edta)CN<sup>2-</sup>. (The signals of edta are too small to be seen.)

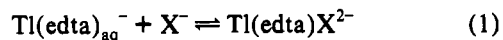
NMR shift for the species Tl(SCN)<sup>2-</sup> is 50.2 ppm (0 °C),<sup>15</sup> and the corresponding value for Tl(edta)(CN)<sup>2-</sup> is 68.0 ppm.

Some spin–spin coupling constants evaluated from the <sup>205</sup>Tl-, <sup>13</sup>C-, and <sup>15</sup>N-NMR spectra are also given in Table I. The spin–spin coupling constant for Tl(edta)(<sup>13</sup>CN)<sup>2-</sup>,  $^1J(^{205}\text{Tl}-^{13}\text{C}) = 10\,479 \pm 30$  Hz, is remarkably large, being close to the upper limit of monoorganothallium(III) range,<sup>32</sup> and only Tl(CN)<sup>2+</sup> and Tl(CN)<sub>2</sub><sup>+</sup> exceed this range. A very strong Tl–CN bond can be concluded from this large  $^1J$  (cf. discussion in ref 14). No coupling constant,  $^2J(^{205}\text{Tl}-\text{S}^{13}\text{CN})$ , could be seen directly in the <sup>13</sup>C spectra. The simplest explanation of this experimental finding is to suppose  $^2J = 0$  Hz, but it does not seem reasonable: (1) The ratio,  $^1J(^{205}\text{Tl}-^{13}\text{C})/^1J(^{205}\text{Tl}-^{13}\text{C})$  is  $10\,479 \text{ Hz}/14\,633 \text{ Hz} \approx 0.7$  for Tl(edta)CN<sup>2-</sup> and TlCN<sup>2+</sup> complexes, respectively. If we suppose the same ratio for the corresponding  $^2J(^{205}\text{Tl}-\text{S}^{13}\text{CN})$  values of the thiocyanato complexes, then the coupling constant for Tl(edta)SCN<sup>2-</sup> would be  $^2J(^{205}\text{Tl}-\text{S}^{13}\text{C}(\text{N})) \sim 0.7 \times 733 \text{ Hz} = 510 \text{ Hz}$ .<sup>15</sup> (2) The half-width of the coordinated SCN<sup>-</sup> signal in <sup>13</sup>C-NMR is significantly broader than that of the free SCN<sup>-</sup> and varies with the temperature. This occurs also in a solution containing [SCN<sup>-</sup>]<sub>tot</sub> = 5 mM, [Tl(edta)]<sub>tot</sub> = 90 mM, and pH = 2.8, in which the thiocyanate is present only in the mixed complex, Tl(edta)(SCN)<sup>2-</sup>. This indicates that some exchange process is in action, leading to “exchange decoupling”. The chemical exchange reaction for this particular situation can

only be the dissociation of the mixed complex; see eq 13 below. Using the rate constants  $k_d = 2.08 \times 10^3 \text{ s}^{-1}$  (–8 °C) and  $k_d = 7.52 \times 10^3 \text{ s}^{-1}$  (+10 °C) obtained by <sup>205</sup>Tl-NMR (see below), and  $\delta_{\text{C}}$ ,  $\Delta\nu_{\text{C}}$ , and  $\Delta\nu^{\circ}_{\text{C}}$  values listed in Table I, one can calculate  $^2J(^{205}\text{Tl}-\text{S}^{13}\text{CN}) = 386 \pm 10$  Hz for the mixed complex by means of complete bandsape analysis to describe the experimental <sup>13</sup>C-NMR line-width values of 312 and 64 Hz at –8 and +10 °C, respectively. The effect of this spin–spin coupling on the kinetic calculations will be discussed later.

The coupling constant  $^2J(^{205}\text{Tl}-\text{C}^{15}\text{N}) = 11$  Hz for Tl(edta)(CN)<sup>2-</sup> was measured by <sup>15</sup>N-NMR.  $^3J(^{205}\text{Tl}-\text{SC}^{15}\text{N})$  for the species Tl(edta)(SCN)<sup>2-</sup> would be larger (say about 30 Hz), if we follow the above used way of reasoning, because the analog values of  $^2J(^{205}\text{Tl}-\text{C}^{15}\text{N})$  and  $^3J(^{205}\text{Tl}-\text{SC}^{15}\text{N})$  are 54 and 143 Hz<sup>15</sup> for Tl(CN)<sup>+</sup> and Tl(SCN)<sup>+</sup>, respectively, but this relatively small spin–spin coupling is certainly “hidden” by chemical exchange. It is noteworthy, that substantial (exchange) broadening was also observed in the <sup>15</sup>N-NMR spectrum of Tl(SCN)<sup>2+</sup> at 0 °C ( $\Delta\nu^{\text{obs}} = 70$  Hz).<sup>15</sup>

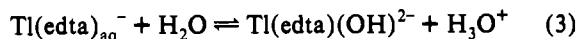
**Determination of Stability Constants.** The stability of the Tl(edta)<sup>-</sup> complex is so high (log  $K = 37.8$ )<sup>5</sup> that this complex does not dissociate at moderate concentrations of an inorganic ligand X<sup>-</sup> in the studied pH range,  $2 \leq \text{pH} \leq 11$ . Accordingly, only the following simple equilibrium has to be considered:<sup>8</sup>



Thus

$$K_{\text{X}} = [\text{Tl}(\text{edta})\text{X}^{2-}]/\{[\text{Tl}(\text{edta})^-][\text{X}^-]\} \quad (2)$$

In addition, at pH > 4, formation of a mixed hydroxo complex occurs:<sup>5</sup>



Accordingly,

$$K_{\text{OH}} = \{[\text{Tl}(\text{edta})(\text{OH})^{2-}][\text{H}_3\text{O}^+]\}/[\text{Tl}(\text{edta})_{\text{aq}}^-] \quad (4)$$

In the case of X<sup>-</sup> = CN<sup>-</sup>, the protonation of the ligand also occurs:



$$K_{\text{HCN}} = [\text{HCN}]/\{[\text{H}^+][\text{CN}^-]\} \quad (6)$$

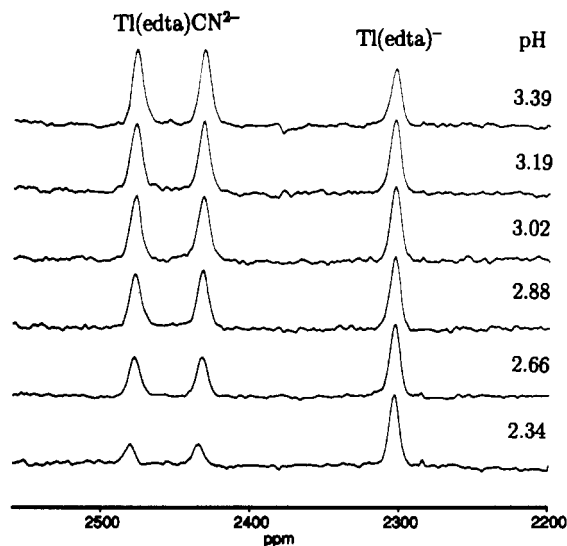
Both reactions 3 and 5 have an effect on reaction 1 via competition for Tl(edta)<sup>-</sup> or CN<sup>-</sup>, respectively. In other words, the increase of pH at pH > 4 decreases the apparent stability of Tl(edta)X<sup>2-</sup> because of the formation of Tl(edta)(OH)<sup>2-</sup> (log  $K_{\text{OH}} = -6.00$ ),<sup>5,8</sup> while at pH < 11 the formation of HCN with decreasing pH has the same effect (log  $K_{\text{HCN}} = 9.09$ )<sup>20</sup>. No protonation of Cl<sup>-</sup>, Br<sup>-</sup>, SCN<sup>-</sup>, and Tl(edta)<sup>-</sup> has to be considered at our experimental conditions (pH ≥ 2.3). The preferable pH region to follow reaction 1 is dependent on the stability constants, (2), (4), and (6), and the total concentrations,  $c_{\text{Tl}(\text{edta})}$  and  $c_{\text{X}}$ . Optimal conditions were determined in preliminary experiments.

In order to investigate the formation of mixed ligand complexes (reaction 1), we gradually changed pH in solutions containing Tl(edta)<sup>-</sup> and X<sup>-</sup> and recorded <sup>13</sup>C- and <sup>205</sup>Tl-NMR spectra. The chemical shift values ( $\delta_{\text{Tl}}$  or  $\delta_{\text{C}}$ ; cf. ref. 20) and/or peak integrals were used to calculate  $K_{\text{X}}$  values according to the actual chemical exchange case, i.e. fast or slow exchange regime depending on the quality of X<sup>-</sup> and the chosen NMR nucleus, <sup>13</sup>C or <sup>205</sup>Tl. The resulting equilibrium constants are presented in Table I.

Note, that the experimental methods chosen for this study (see above, under pH Measurements) give so called stoichiometric equilibrium constants, i.e. based on concentrations and *not* activities.

**(a) Tl(edta)<sup>-</sup>-CN<sup>-</sup> System.** This system was found to be in slow exchange regime on both <sup>13</sup>C- and <sup>205</sup>Tl-NMR time scales.

(32) (a) Hinton, J. F.; Metz, K. R.; Briggs, R. W. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: London, 1982; Vol. 13, p 211. (b) Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: London, 1978, pp 302–303.



**Figure 2.**  $\text{Tl}(\text{edta})\text{CN}^{2-}$  system. 230-MHz  $^{205}\text{Tl}$ -NMR spectra of an aqueous solution containing 0.010 M  $\text{Tl}(\text{edta})^-$ , 0.010 M NaCN (enriched to 99% in  $^{13}\text{C}^-$ ), and 1 M  $\text{NaClO}_4$  at different pH values and 25 °C.

Typical spectra are shown in Figures 1 and 2. The peaks at  $\delta_{\text{C}} = 113.5$  and 116.2 ppm belong to the proton-coupled  $^{13}\text{C}$  signal of HCN;<sup>14</sup> the signals at  $\delta_{\text{C}} = 98.6$  and 202.4 ppm and  $\delta_{\text{C}} = 99.0$  and 201.9 ppm were assigned to the  $^{13}\text{C}$ -Tl spin-spin-coupled  $^{205}\text{Tl}$  and  $^{203}\text{Tl}$  isotomers, respectively, of the  $\text{Tl}(\text{edta})\text{CN}^{2-}$  complex. The spin-spin coupling constant is  $J(^{205}\text{Tl}-^{13}\text{C}) = 10\,479 \pm 30$  Hz. The same constant can be found from  $^{205}\text{Tl}$ -NMR spectra (Figure 2), where the peaks at  $\delta_{\text{Tl}} = 2440.6$  and 2485.6 ppm represent the doublet of  $\text{Tl}(\text{edta})\text{CN}^{2-}$  (99% enriched in  $^{13}\text{C}^-$ ); a singlet at  $\delta_{\text{Tl}} = 2301$  ppm represents  $\text{Tl}(\text{edta})^-$ .

The stability constant,  $K_{\text{CN}}$ , was determined by least-squares refinement to the  $^{205}\text{Tl}$ - and  $^{13}\text{C}$ -NMR peak integrals (from the spectra in Figures 1 and 2) and mass balance equations:

$$c_{\text{Tl}} = [\text{Tl}(\text{edta})^-] + [\text{Tl}(\text{edta})(\text{OH})^{2-}] + [\text{Tl}(\text{edta})(\text{CN})^{2-}] \quad (7)$$

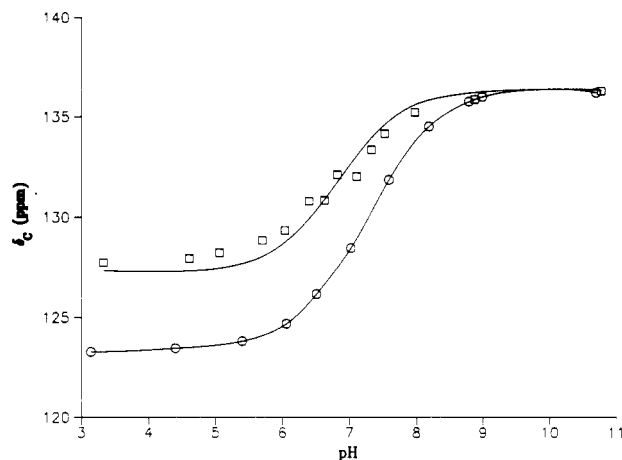
$$c_{\text{CN}} = [\text{HCN}] + [\text{CN}^-] + [\text{Tl}(\text{edta})(\text{CN})^{2-}] \quad (8)$$

$[\text{H}^+]$  was determined experimentally; the stability constants  $\log K_{\text{OH}} = -6.00^5$  and  $\log K_{\text{HCN}} = 9.09^{20}$  were held constant during the refinement. The calculation gave  $\log K_{\text{CN}} = 8.72 (\pm 0.03 = \sigma)$ , which means that  $\text{Tl}(\text{edta})(\text{CN})^{2-}$  is the most stable of the known mixed complexes  $\text{Tl}(\text{edta})\text{X}^{2-}$ ; the value of  $\log K_{\text{CN}}$  is larger than  $\log K_1 = 5.9 (\pm 0.2)^8$  by almost 3 orders of magnitude. This high stability of  $\text{Tl}(\text{edta})(\text{CN})^{2-}$  could be predicted from the stability of  $\text{Tl}(\text{CN})_{n-3-n}$  complexes, which are the most stable known monodentate complexes of Tl(III).<sup>14</sup> The value of  $\log K_{\text{CN}}$  is close to  $\log K_4 = 7.44$  (the stepwise stability constant for the species  $\text{Tl}(\text{CN})_4^-$ ;  $I = 1$  M  $\text{NaClO}_4 + 3$  M  $\text{LiClO}_4$ ).<sup>14</sup> The same similarity has been found for  $\text{X}^- = \text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ .<sup>8</sup> It is noteworthy, that even if the mixed complex,  $\text{Tl}(\text{edta})(\text{CN})^{2-}$ , is very stable, no formation of  $\text{Tl}(\text{edta})(\text{CN})_2^{3-}$  has been found. Apparently, only one monodentate ligand  $\text{X}^-$  can be coordinated to the  $\text{Tl}(\text{edta})_{\text{aq}}^-$  without replacement of donor atom(s) of the edta ligand.

**(b)  $\text{Tl}(\text{edta})^-$ - $\text{SCN}^-$  System.** The fast exchange regime governs  $^{13}\text{C}$ -NMR spectra of  $\text{SCN}^-$  and  $\text{Tl}(\text{edta})\text{SCN}^{2-}$ . Hence, the chemical shift of the time-averaged signal ( $\delta_{\text{C}}$ ) is a function of the individual chemical shifts ( $\delta_{\text{SCN}}$  and  $\delta_{\text{Tl}(\text{edta})\text{SCN}}$ ) and the molar fractions ( $p_{\text{SCN}}$  and  $p_{\text{Tl}(\text{edta})\text{SCN}}$ ) of the free and coordinated  $\text{SCN}^-$ :

$$\delta_{\text{C}} = \delta_{\text{SCN}}p_{\text{SCN}} + \delta_{\text{Tl}(\text{edta})\text{SCN}}p_{\text{Tl}(\text{edta})\text{SCN}} \quad (9)$$

The ratio of the two species was varied by changing pH at constant



**Figure 3.**  $\text{Tl}(\text{edta})^-$ - $\text{SCN}^-$ - $\text{OH}^-$  system.  $^{13}\text{C}$ -NMR chemical shift of the time-averaged signal of  $\text{SCN}^-$  as a function of pH. The symbols represent experimental values for two series of solutions: ( $\square$ )  $[\text{Tl}(\text{edta})^-]_{\text{tot}} = 0.0106$  M,  $[\text{SCN}^-]_{\text{tot}} = 0.0118$  M; ( $\circ$ )  $[\text{Tl}(\text{edta})^-]_{\text{tot}} = 0.0400$  M,  $[\text{SCN}^-]_{\text{tot}} = 0.0300$  M. The lines were calculated using  $\log K_{\text{SCN}} = 2.70$  and  $\delta_{\text{Tl}(\text{edta})\text{SCN}} = 121.6$  ppm (see text).

$c_{\text{SCN}}/c_{\text{Tl}(\text{edta})}$  ( $c_{\text{SCN}} = 0.0118$  M,  $c_{\text{Tl}(\text{edta})} = 0.0106$  M and  $c_{\text{SCN}} = 0.0300$  M,  $c_{\text{Tl}(\text{edta})} = 0.0400$  M; see Figure 3) or changing the ratio  $c_{\text{SCN}}/c_{\text{Tl}(\text{edta})}$  at  $\text{pH} = 2.8 \pm 0.1$ . The mixed-ligand stability constant  $K_{\text{SCN}}$  and  $\delta_{\text{Tl}(\text{edta})\text{SCN}}$  were least-squares fitted to the chemical shift values  $\delta_{\text{C}}$  in eq 9 and to the mass-balance equations, similar to eqs 7 and 8.  $\delta_{\text{SCN}}$  was determined in a separate measurement, and pH values were measured with a glass electrode,  $\log K_{\text{OH}} = -6.00$ ;<sup>5</sup> these parameters were kept constant during the refinements. The best fit was found for  $\log K_{\text{SCN}} = 2.70 (\pm 0.09)$  and  $\delta_{\text{Tl}(\text{edta})\text{SCN}} = 121.6$  ppm. Experimental  $\delta_{\text{C}}$  values are shown as a function of pH together with the calculated curves (Figure 3).

The stability constant of the mixed complex  $\text{Tl}(\text{edta})(\text{SCN})^{2-}$  is lower than the corresponding value for the cyano complex,  $\text{Tl}(\text{edta})(\text{CN})^{2-}$ , by 6 orders of magnitude. The stability constant for the complex  $\text{Tl}(\text{SCN})^{2+}$  is not known, but it is interesting to note that the estimated difference between the stability constants for the complexes  $\text{Tl}(\text{SCN})^{2+}$  and  $\text{Tl}(\text{CN})^{2+}$ <sup>14,15</sup> is about the same. The value of  $\log K_{\text{SCN}} = 2.70$  is between the values for the chloro ( $\log K_{\text{Cl}} = 2.3^8$ ) and the bromo mixed complex ( $\log K_{\text{Br}} = 3.5^8$ ), suggesting a relatively "soft" character<sup>27</sup> of  $\text{SCN}^-$ , just between  $\text{Cl}^-$  and  $\text{Br}^-$ . Mercury(II), which is isoelectronic to thallium(III) but somewhat "softer" does not show such difference; the values of  $\log \beta_{1-4}$  for  $\text{Hg}(\text{SCN})_{1-4}$  and  $\text{HgBr}_{1-4}$ , respectively, are close to each other.<sup>33</sup>

$^{205}\text{Tl}$ -NMR spectra are governed by slow exchange regime at 25 °C (see Figure 4). Hence, the peak integrals could be used to calculate the stability constant, but were not used since the integration of the broad signals could not be performed with high accuracy, compared to the  $^{13}\text{C}$ -NMR chemical shift measurements (see above).

**(c)  $\text{Tl}(\text{edta})^-$ - $\text{Cl}^-$  System.** The mixed ligand stability constant,  $K_{\text{Cl}}$ , has been measured earlier by the potentiometric technique.<sup>8</sup> The present study offered an easy way to check this value. The fast exchange regime governs  $^{205}\text{Tl}$ -NMR spectra of the  $\text{Tl}(\text{edta})^-$ - $\text{Cl}^-$  system. Hence, the chemical shift of the time-averaged signal ( $\delta_{\text{Tl}}$ ) is a function of the individual chemical shifts ( $\delta_{\text{Tl}(\text{edta})}$  and  $\delta_{\text{Tl}(\text{edta})\text{Cl}}$ ) and the molar fractions ( $p_{\text{Tl}(\text{edta})}$  and  $p_{\text{Tl}(\text{edta})\text{Cl}}$ ) of  $\text{Tl}(\text{edta})^-$  and  $\text{Tl}(\text{edta})(\text{Cl})^{2-}$ :

$$\delta_{\text{Tl}} = \delta_{\text{Tl}(\text{edta})}p_{\text{Tl}(\text{edta})} + \delta_{\text{Tl}(\text{edta})\text{Cl}}p_{\text{Tl}(\text{edta})\text{Cl}} \quad (10)$$

The ratio of the two species was varied by varying  $c_{\text{Cl}}/c_{\text{Tl}(\text{edta})} = 0.5$ –20 at  $c_{\text{Tl}(\text{edta})} = 10$  mM and  $\text{pH} = 3.4 (\pm 0.1)$ . The mixed-

(33) Högföldt, E. *Stability Constants of Metal-Ion Complexes, Part A*; IUPAC Chemical Data Series 21, Pergamon Press: Oxford, 1982; p 91.

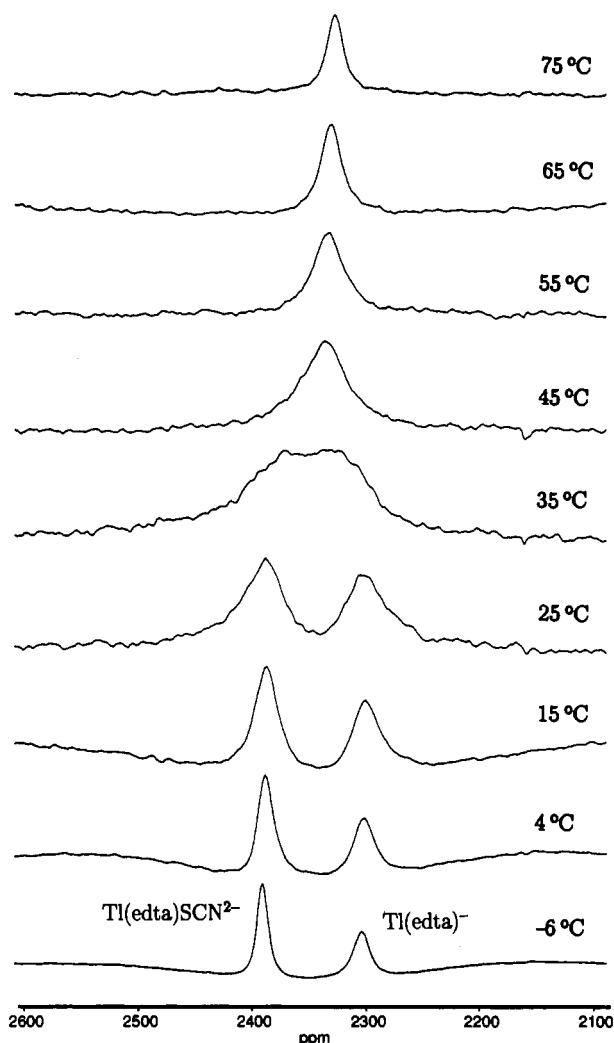
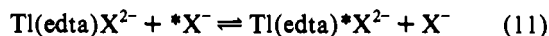


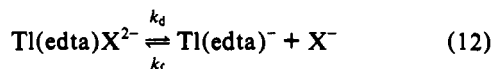
Figure 4. Tl(edta)-SCN<sup>-</sup> system. 230-MHz <sup>205</sup>Tl-NMR spectra of aqueous solutions containing 0.020 M Tl(edta)<sup>-</sup>, 0.012 M NaSCN (enriched to 75% in S<sup>13</sup>CN<sup>-</sup>), and 1 M NaClO<sub>4</sub> at pH = 2.70 and at different temperatures.

ligand stability constant,  $K_{Cl}$ , was calculated from the measured chemical shift values,  $\delta_{Tl}$ , for the individual samples using eq 12 and mass balance equations.  $\delta_{Tl(edta)Cl}$  was determined independently at large excess of Cl<sup>-</sup>; also  $\delta_{Tl(edta)}$  was obtained from independent measurements (see Table I). From five experimental points,  $\log K_{Cl} = 2.6 \pm 0.1$ , in reasonable agreement with the potentiometry ( $2.3 \pm 0.1^8$ ).

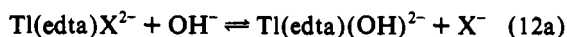
**Equilibrium Dynamics.** Line widths of the NMR signals were found to vary with the composition of the solutions (both <sup>13</sup>C- and <sup>205</sup>Tl-NMR spectra were recorded for X<sup>-</sup> = SCN<sup>-</sup> and CN<sup>-</sup>, but only <sup>205</sup>Tl-NMR spectra for X<sup>-</sup> = Cl<sup>-</sup> and Br<sup>-</sup>). This broadening can be attributed to several exchange reactions, generally written as follows:



The exchange of X<sup>-</sup> might occur via dissociation



or, for example, via a reaction with hydroxyl ion



The rate laws for the chemical exchange in the systems Tl(edta)-X<sup>-</sup>-H<sub>2</sub>O, in the ionic medium of 1 M NaClO<sub>4</sub>, were evaluated by using <sup>205</sup>Tl- and/or <sup>13</sup>C-NMR as follows.

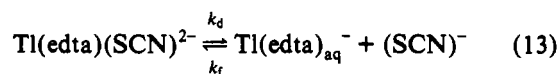
**(I) <sup>205</sup>Tl NMR Studies.** If not stated otherwise, the signal of the mixed complex, Tl(edta)X<sup>2-</sup>, was used for the kinetic

calculations. This was done to simplify the reasoning and because of an additional complication concerning the Tl(edta)<sup>-</sup> signal (see below).

**(a) Tl(edta)<sup>-</sup>-CN<sup>-</sup> System.** In this case we observe slow exchange at the current experimental conditions (Figure 2). No exchange broadening of <sup>205</sup>Tl peaks was observed for the Tl(edta)<sup>-</sup>-CN<sup>-</sup> system at room temperature. Considering about 300 Hz as the smallest observable exchange broadening for the relatively broad signals,  $k_{obs} \leq 1 \times 10^3 \text{ s}^{-1}$  can be estimated.

The lower limit of the pseudo-first-order rate constant can be evaluated even more precisely using <sup>13</sup>C-NMR spectra of the edta ligand in the complexes Tl(edta)<sup>-</sup> and Tl(edta)(CN)<sup>2-</sup>. The difference between the corresponding chemical shifts of the carbonyl carbon signals is 0.18 ppm (or 18 Hz). The chemical exchange reaction was found to be slow on the <sup>13</sup>C-NMR time scale; i.e. the signals of Tl(edta)<sup>-</sup> and Tl(edta)CN<sup>2-</sup> appeared separately, and no broadening was observed (0.05 M NaTl(edta) + 0.025 M NaCN, 1 M NaClO<sub>4</sub> in D<sub>2</sub>O, pH = 2.8). For <sup>13</sup>C-NMR the lowest detectable change in the line width is about  $\Delta\nu_C \sim 1 \text{ Hz}$ ; hence, the upper limit of the rate constant is  $k_{obs} < 3 \text{ s}^{-1}$ , smaller than the corresponding values for SCN<sup>-</sup> and Br<sup>-</sup> systems (see below and Table II, where the rate constants are summarized).

**(b) Tl(edta)<sup>-</sup>-SCN<sup>-</sup> System.** At room temperature, the chemical exchange was "slow" on the actual <sup>205</sup>Tl-NMR time scale. Typical spectra are shown in Figure 4. The signal of the mixed complex, Tl(edta)(SCN)<sup>2-</sup>, at  $\delta_{Tl} = 2385 \text{ ppm}$  has a line width,  $\Delta\nu_{obs,Tl} = 7700 \pm 500 \text{ Hz}$  (at 25 °C), which does not change significantly when pH,  $c_{Tl(edta)}$  or  $c_{SCN}$  are varied, as long as the slow exchange regime governs the spectra. The nonexchange line width for this complex could be measured in the presence of large excess of SCN<sup>-</sup>,  $\Delta\nu_{Tl} = 1200 \text{ Hz}$  (see Table I). Thus, the exchange broadening of this signal is  $\Delta\nu = \Delta\nu_{obs,Tl} - \Delta\nu_{Tl} = 6500 \text{ Hz}$ , leading to the pseudo-first-order rate constant  $k_{obs} = -d[Tl(edta)(SCN)^{2-}]/\{[Tl(edta)(SCN)^{2-}]dt\} = \pi(\Delta\nu) = 2.04 (\pm 0.16) \times 10^4 \text{ s}^{-1}$ . The rate law is simple, because no second-order term was found. This first-order rate constant can be attributed to the dissociation of the mixed complex, Tl(edta)(SCN)<sup>2-</sup>, as follows:



i.e.  $k_{obs} = k_d$ . The temperature dependence of the <sup>205</sup>Tl-NMR spectra can be seen in Figure 4. The exchange regime turns to fast on the actual time scale at 45 °C. For this and higher temperatures, the values of  $k_{obs}$  were calculated using the Piette-Anderson formula.<sup>34</sup> The temperature dependence of the individual chemical shifts was measured from the slow exchange spectra,  $\Delta\delta/\Delta t = -0.15$  and  $-0.19 \text{ (ppm/K)}$  for Tl(edta)<sup>-</sup> and Tl(edta)(SCN)<sup>2-</sup>, respectively, and were linearly extrapolated to the higher temperature values. The Arrhenius plot is shown in Figure 5. The activation parameters, calculated by least-squares fitting, are  $\Delta H^{\ddagger} = 47 (\pm 2 = \sigma) \text{ kJ mol}^{-1}$  and  $\Delta S^{\ddagger} = -6 (\pm 6 = \sigma) \text{ J mol}^{-1} \text{ K}^{-1}$ .

**(c) Tl(edta)<sup>-</sup>-Cl<sup>-</sup> System.** Time-averaged <sup>205</sup>Tl-NMR signals (i.e. fast exchange regime) without exchange broadening were observed in this system. Here, the chemical shift difference between the signals of Tl(edta)Cl<sup>2-</sup> and Tl(edta)<sup>-</sup> is 7.8 ppm or 1800 Hz (cf. Table I). Considering the smallest detectable exchange broadening,  $\Delta\nu \geq 300 \text{ Hz}$ , and  $p_a = p_b = 0.5$ , the limiting value of  $k_{obs} \geq 1.7 \times 10^4 \text{ s}^{-1}$  can be calculated by the Piette-Anderson formula.<sup>34</sup>

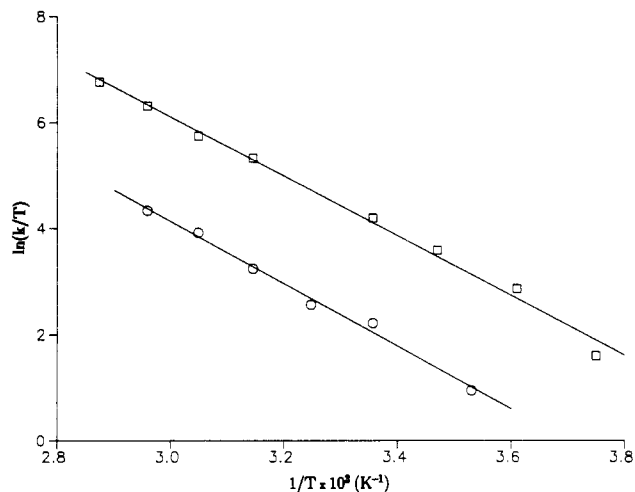
**(d) Tl(edta)<sup>-</sup>-Br<sup>-</sup> System.** Similar to that in Tl(edta)<sup>-</sup>-SCN<sup>-</sup> system at low temperatures, the chemical exchange at room temperature is "slow" on the <sup>205</sup>Tl-NMR time scale. The rate

(34) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982; p 17.

**Table II.** Kinetic Data for X Ligand Exchange Reactions Involving Tl(edta)X<sup>2-</sup> at 25 °C

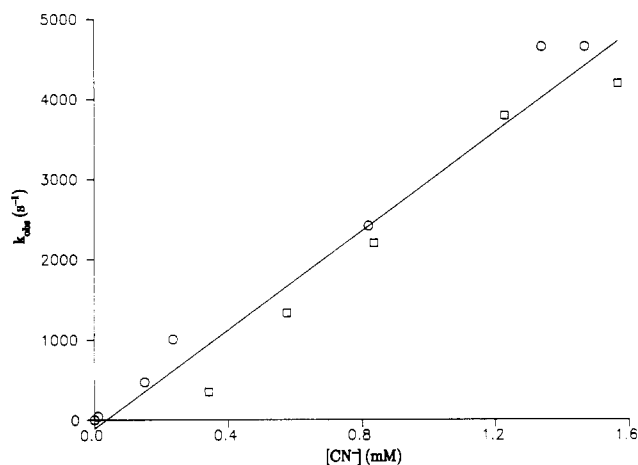
complex	$k_d^a$ (s <sup>-1</sup> )	$k_2^c$ (M <sup>-1</sup> s <sup>-1</sup> )	$k_d^f$ (s <sup>-1</sup> )	$k_f^d$ (M <sup>-1</sup> s <sup>-1</sup> )	$k_w^e$ (s <sup>-1</sup> )	$k_w^f$ (s <sup>-1</sup> )
Tl(edta)Cl <sup>2-</sup>	$\geq 1.7 \times 10^4$			$\geq 3.4 \times 10^6$	$\geq 4.6 \times 10^7$	
Tl(edta)Br <sup>2-</sup>	$(2.7 \pm 0.3) \times 10^3$			$8.6 \times 10^6$	$1.2 \times 10^8$	
Tl(edta)CN <sup>2-</sup>	$< 3^b$	$(1.5 \pm 0.3) \times 10^6$	$(-1 \pm 6) \times 10^2$	$< 1.6 \times 10^9$	$\leq 3.5 \times 10^{10}$	$1.3 \times 10^8$
Tl(edta)SCN <sup>2-</sup>	$(2.0 \pm 0.2) \times 10^4$	$(3.0 \pm 0.5) \times 10^6$	$(2.7 \pm 0.6) \times 10^4$	$1.0 \times 10^7$	$1.3 \times 10^8$	$2.5 \times 10^8$

<sup>a</sup> Measured for <sup>205</sup>Tl-NMR signal of Tl(edta)X<sup>2-</sup>. <sup>b</sup> Measured for <sup>13</sup>C-NMR carbonyl signal of Tl(edta)<sup>-</sup>. <sup>c</sup> Measured for <sup>13</sup>C-NMR signal of <sup>13</sup>CN<sup>-</sup> or <sup>13</sup>CSCN<sup>-</sup>. <sup>d</sup>  $k_f = k_d K_X$ ;  $k_d$  values measured as in footnotes a and b. <sup>e</sup>  $k_w = k_f / K_{os}^{-1,-1}$ ;  $K_{os}^{-1,-1} = 0.074 \text{ M}^{-1}$  (see text). <sup>f</sup>  $k_w = k_2 / K_{os}^{-2,-1}$ ;  $K_{os}^{-2,-1} = 0.012 \text{ M}^{-1}$  (see text).

**Figure 5.** Arrhenius plot for mixed complex formation (reaction 16) in the systems Tl(edta)-SCN<sup>-</sup> (□) and Tl(edta)-Br<sup>-</sup> (○).

law for the Tl(edta)-Br<sup>-</sup> system appears to be similar to that for the Tl(edta)-SCN<sup>-</sup> system. The signal of the mixed complex, Tl(edta)Br<sup>2-</sup>, at  $\delta_{\text{Tl}} = 1883 \text{ ppm}$  has a line width  $\Delta\nu^{\text{obs}} = 2070 \pm 100 \text{ Hz}$  at 25 °C, which does not change significantly with pH,  $c_{\text{Tl(edta)}}$ , or  $c_{\text{Br}^-}$ . The nonexchange line width of Tl(edta)Br<sup>2-</sup> was measured to be 1200 Hz at -5 °C, so the exchange broadening is  $\Delta\nu = 870 \pm 100 \text{ Hz}$ . The pseudo-first-order rate constant  $k_{\text{obs}} = \pi(\Delta\nu) = -d[\text{Tl(edta)Br}^{2-}]/\{[\text{Tl(edta)Br}^{2-}]dt\} = 2.7 (\pm 0.3) \times 10^3 \text{ s}^{-1}$ , and  $k_{\text{obs}} = k_d$ . This rate constant is smaller than  $k_d^{\text{SCN}^-}$ ; i.e. the dissociation of Tl(edta)Br<sup>2-</sup> is slower than that of Tl(edta)(SCN)<sup>2-</sup>. No coalescence of the signals appears until 65 °C, so the "slow" exchange formula was used for all the <sup>205</sup>Tl-NMR spectra in the bromide system in order to obtain the rate constant values for the Arrhenius plot (Figure 5). The activation parameters are  $\Delta H^\ddagger = 49 (\pm 2 = \sigma) \text{ kJ mol}^{-1}$  and  $\Delta S^\ddagger = -15 (\pm 8 = \sigma) \text{ J mol}^{-1} \text{ K}^{-1}$ , i.e. not significantly different from the activation parameters for the corresponding reaction of the thiocyanato mixed complex, reaction 13.<sup>35</sup>

(II) <sup>13</sup>C NMR Studies. The simple rate laws derived from the <sup>205</sup>Tl-NMR spectra,  $k_{\text{obs}} = k_d$ , represent only one part of the possible ligand exchange paths. There is another type of reaction involving X<sup>-</sup> as reactant (eq 11) which has no effect on the <sup>205</sup>Tl-NMR spectra, since the chemical surrounding for this nucleus is not changed in the reaction. Fortunately, in the cases of Tl(edta)CN<sup>2-</sup> and Tl(edta)SCN<sup>2-</sup>, <sup>13</sup>C-NMR offered enough sensitivity to study this kind of exchange processes. On the other hand, for Tl(edta)Cl<sup>2-</sup> and Tl(edta)Br<sup>2-</sup> the corresponding studies

**Figure 6.** Tl(edta)-CN<sup>-</sup> system. Dependence of pseudo-first-order rate constants (obtained from <sup>13</sup>C-NMR line widths of the Tl(edta)CN<sup>2-</sup> signal at 25 °C) on [CN<sup>-</sup>] in two series of solutions: (1) [Tl(edta)]<sub>tot</sub> = 6 mM, [CN<sup>-</sup>]<sub>tot</sub> = 12 mM, pH = 7.5–8.8; pH = 3.24 for the point at the origin (○); (2) [CN<sup>-</sup>]<sub>tot</sub>/[Tl(edta)]<sub>tot</sub> = 2, [Tl(edta)]<sub>tot</sub> = 3.0–10 mM, pH = 8.30 ± 0.15 (□).

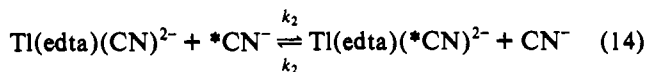
are not possible because of the fast quadrupolar relaxation of the NMR-active isotopes of Cl and Br.

(a) Tl(edta)-CN<sup>-</sup> System. No exchange broadening was found at different excess of HCN at pH ≤ 5–6. No useful experiments could be made in the unbuffered pH-region, about 6–7.5 (cf. the recent study of the proton exchange of HCN<sup>36</sup>). Since the protonation constant (eq 6) of CN<sup>-</sup> in 1 M NaClO<sub>4</sub> is  $\log K_{\text{HCN}} = 9.09$ ,<sup>20</sup> for pH ≥ 7.5 and at a suitably large concentration of free CN<sup>-</sup> the system is buffered enough to measure pH. The pH values were finally checked by means of <sup>13</sup>C-NMR (see Experimental Section, pH Measurements). Increasing the pH in a solution of 0.03 M Tl(edta)<sup>-</sup> containing 0.06 M Na<sup>13</sup>CN, at pH ≈ 8 all of the signals become very broad and practically escape observation, but after dilution (3–10 times) the signals can be found again at their original position, and the line widths vary with the concentration of the mixed complex, the concentration of CN<sup>-</sup>, and/or pH. The exchange broadening was preferably measured on the signal of the Tl(edta)(CN)<sup>2-</sup> at  $\delta_{\text{C}} = 202 \text{ ppm}$ , which is far from the signal of the free cyanide (rather than the signal at 98 ppm, which overlaps with the latter one at higher CN<sup>-</sup> concentrations) (cf. Figure 1). At  $\delta_{\text{C}} = 201.6 \text{ ppm}$ , the <sup>205</sup>Tl-coupled <sup>13</sup>C signal appears, which can overlap with the <sup>205</sup>Tl-coupled <sup>13</sup>C signal and has some effect on the measured line width. The individual line width for the latter signal was calculated from the measured value using a correction, based on a model calculation with two partially overlapping Lorentzian curves with the same line width. The resulting <sup>13</sup>C-NMR line width (corrected for the nonexchange line width) was then multiplied by 2 to obtain  $\Delta\nu^{\text{obs}}$ , because of the doublet pattern of the signal. The values of  $k_{\text{obs}} (= \pi(\Delta\nu^{\text{obs}}))$  were now plotted against [CN<sup>-</sup>] in Figure 6. The concentration of the free cyanide ion, [CN<sup>-</sup>], was calculated from the pH value in combination with the known stability constant of HCN in the actual ionic

(35) In <sup>205</sup>Tl-NMR spectra there is a significant broadening of the Tl(edta)<sup>-</sup> signal at lower temperatures, where no broadening of the signal of Tl(edta)Br<sup>2-</sup> is observed. This experimental finding is probably related to a change in the <sup>1</sup>H-<sup>205</sup>Tl spin-spin coupling pattern, caused by an internal rearrangement within the Tl(edta)<sup>-</sup> complex. The <sup>205</sup>Tl signal of Tl(edta)<sup>-</sup> in the absence of bromide also shows the same broadening at lower temperatures (2200 Hz at +10 °C and 3140 Hz at -5 °C), indicating an exchange process independent of the mixed complex. On the other hand, this broadening does not appear in the case of Tl(edta)-SCN<sup>-</sup> system. A possible explanation is that the reaction 13 is so fast even at -5 °C that the effect of the other, independent exchange process is hidden. Detailed study of this phenomenon is outside the scope of this paper.

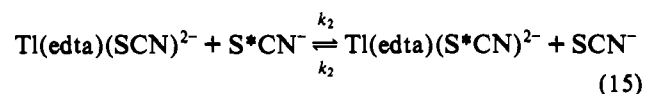
(36) Bányai, I.; Blixt, J.; Glaser, J.; Tóth, I. *Acta Chem. Scand.* **1992**, *46*, 142.

medium,  $\log K_{\text{HCN}} = 9.09$ . Very long accumulation times were required in order to obtain good signal-to-noise ratio in these dilute solutions giving broad NMR signals ( $\approx 10$ –600 Hz) in the two-site exchange system, both of the sites coupled (HCN,  $^1J(\text{H}-^{13}\text{C}) = 270.6$  Hz,<sup>14</sup> Tl(edta)(CN)<sup>2-</sup>,  $^1J(^{205}\text{Tl}-^{13}\text{C}) = 10\,479$  Hz; see Table I). The experimental results can be described by a straight line with a slope of  $3.0 (\pm 0.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and an intercept of  $-1 (\pm 2) \times 10^2 \text{ s}^{-1}$ . The rate law can now be written as  $k_{\text{obs}} = 2k_2[\text{CN}^-]$ , according to the following reaction:



The straight line contains experimental points measured at different values of pH,  $c_{\text{Tl}(\text{edta})}$  and  $c_{\text{NaCN}}$ , so that virtually no other reactions have to be considered. In the present system the proton transfer reactions of HCN are relatively fast;<sup>36,37</sup> the equilibrium in (5) is established so rapidly during the ligand exchange reaction (14) that it cannot be the rate-determining step. This rate law is consistent with the experimental results discussed above in the section <sup>205</sup>Tl NMR Studies, and  $k_d < 3 \text{ s}^{-1}$  obtained previously using the <sup>13</sup>C-NMR signals of coordinated edta (see above) is in agreement with the zero intercept obtained from Figure 6.

(b) Tl(edta)<sup>-</sup>–(SCN)<sup>-</sup> System. When discussing the determination of the stability constant of Tl(edta)(SCN)<sup>2-</sup>, we have mentioned that “fast” exchange with substantial exchange broadening was found on the <sup>13</sup>C-NMR time scale. Our attempts to describe the exchange processes as a simple, two-site, uncoupled spin system were not successful: the  $k_{\text{obs}}$  vs [SCN<sup>-</sup>] curve gave intercept  $< 0$ , which is in contrast to the rate law measured by <sup>205</sup>Tl-NMR, and it is chemically nonsense. Changing our model to a two site system, where one of the sites is spin–spin coupled, we could present a possible description of the exchange dynamics using complete line-shape analysis. The crucial point of the calculation was already mentioned above: direct measurement of the  $^2J(^{205}\text{Tl}-\text{S}^{13}\text{CN})$  spin–spin coupling constant was not possible, since the solution containing the complex Tl(edta)(SCN)<sup>2-</sup> was frozen at higher temperature than what would be necessary to slow down reaction 12 and hence avoid the exchange averaging of the spin–spin coupling.  $^2J(^{205}\text{Tl}-\text{S}^{13}\text{CN}) = 386$  Hz was calculated by simulation of the <sup>13</sup>C-NMR spectra using the rate constant values obtained from <sup>205</sup>Tl-NMR at two temperatures (see above). Using the independently measured chemical shift, nonexchange line widths (Table I), populations calculated from the equilibrium constant, and the total concentrations, NMR spectra were simulated<sup>38</sup> with different rate constant values and were compared to the experimental ones. Both the line width and the chemical shift had to agree within  $\pm 1$  Hz and  $\pm 0.2$  ppm, respectively, for the experimental and the calculated spectra, before the fit was accepted. The calculated  $k_{\text{obs}}^{\text{C}}$  values are plotted versus [SCN<sup>-</sup>] in Figure 7. The straight line gives intercept =  $2.7 (\pm 0.2) \times 10^4 \text{ s}^{-1}$  and slope =  $6.1 (\pm 0.3) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ , resulting in the rate law  $k_{\text{obs}}^{\text{C}} = k_d + 2k_2[\text{SCN}^-]$ . These values can be attributed to the rate constant  $k_d$  of reaction 13 and  $2k_2^{\text{SCN}}$  of the following reaction:



The <sup>13</sup>C-NMR results are consistent with the rate law obtained by <sup>205</sup>Tl-NMR; i.e., the only second-order reaction involved in the ligand exchange system is reaction 15.

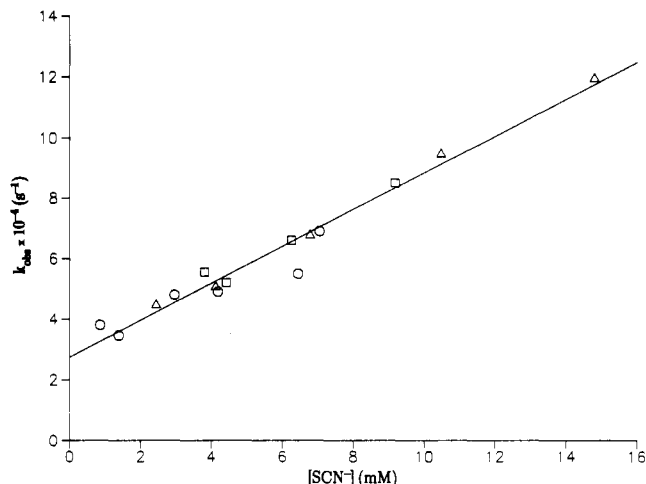


Figure 7. Tl(edta)<sup>-</sup>–SCN<sup>-</sup> system. Dependence of pseudo-first-order rate constant (obtained from <sup>13</sup>C-NMR line widths of the Tl(edta)SCN<sup>2-</sup> signal at 25 °C) on [SCN<sup>-</sup>] in three series of solutions: (1) [Tl(edta)<sup>-</sup>]<sub>tot</sub> = 10 mM, [SCN<sup>-</sup>]<sub>tot</sub> = 5.0–15 mM, pH = 2.7 (O); (2) [Tl(edta)<sup>-</sup>]<sub>tot</sub> = 40 mM, [SCN<sup>-</sup>]<sub>tot</sub> = 30 mM, pH = 3.3–6.7 (□); (3) [Tl(edta)<sup>-</sup>]<sub>tot</sub> = 30 mM, [SCN<sup>-</sup>]<sub>tot</sub> = 20–40 mM, pH = 2.7 (Δ).

Table II summarizes the values/limits of the rate constants, together with some derived kinetic parameters.

**Structure of Tl(edta)CN<sup>2-</sup> in the Solid State.** The structure of the Tl(edta)CN<sup>2-</sup> complex in the crystals of Na<sub>2</sub>Tl(edta)CN·3H<sub>2</sub>O is shown in Figure 8. The fractional atomic coordinates together with the isotropic temperature factors for the non-hydrogen atoms are given in Table III. The thallium atom is coordinated in the way usual for metal-edta complexes, i.e. in an “edta-basket” formed by two nitrogens and four oxygens (the latter lying in a tetrahedrally distorted plane, i.e. the angles O1–Tl–O2 and O3–Tl–O4 are not equal to 180°) with the bond distances (in Å): Tl–O1 = 2.36 (2), Tl–O2 = 2.29 (2), Tl–O3 = 2.43 (2), Tl–O4 = 2.35 (2), Tl–N1 = 2.41 (2), and Tl–N2 = 2.41 (2). One of the halves of edta (with oxygen atoms O2 and O4) has Tl–O distances that are 0.07–0.08 Å shorter than the corresponding Tl–O distances for the other half (O1 and O3).

Due to the relatively large size of thallium (ionic radius = 0.95 Å), edta is not able to encircle it completely. This leaves room for coordination of the cyanide, resulting in a total coordination number of 7. The Tl–CN distance, 2.14 (3) Å, can be compared to the corresponding distance determined by large-angle X-ray scattering on concentrated aqueous solution: 2.11 Å in Tl(CN)<sub>2</sub><sup>+</sup> and 2.19 Å in Tl(CN)<sub>4</sub><sup>-</sup>.<sup>39</sup> The Tl–C11–N3 angle is 171 (3)°. The coordination of thallium in Na<sub>2</sub>Tl(edta)CN·3H<sub>2</sub>O is similar to that in CaTl(edta)(OH)<sup>-</sup>·3H<sub>2</sub>O.<sup>26</sup>

Small metal ions, like, e.g., Co<sup>3+</sup> (ionic radius = 0.63 Å), can be completely encircled by edta,<sup>40</sup> leading to the coordination number of 6. Slightly larger ions are not completely inside the edta basket and hence seven-coordination becomes possible, as e.g. for Fe<sup>3+</sup>, Mg<sup>2+</sup>, Ti<sup>4+</sup>, and Mn<sup>2+</sup> (radii = 0.64, 0.65, 0.68, and 0.80 Å, respectively).<sup>41–44</sup> There is a correlation between the ionic radius of the metal ion and the distance from the metal up to the oxygen-plane (cf. Figure 8). Hence, Fe<sup>3+</sup> is 0.15–0.20 Å below the plane, and Mg<sup>2+</sup> is 0.21 Å, Ti<sup>4+</sup> is 0.12 Å, Mn<sup>2+</sup> is 0.10 Å and Ti<sup>3+</sup> = 0.08 Å below the plane (calculated from parameters given in refs 41–44), respectively; since in these cases X = H<sub>2</sub>O,

(37) (a) Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 7117. (b) Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 7126. (c) Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 7135.  
(38) (a) Reeves, L. W.; Shaw, K. N. *Can. J. Chem.* **1970**, *48*, 3641. (b) Chan, S. O.; Reeves, L. W. *J. Am. Chem. Soc.* **1973**, *95*, 670.

(39) Blixt, J.; Glaser, J.; Persson, I.; Sandström, M. Preliminary results. (40) Weakliem, H. A.; Hoard, J. L. *J. Am. Chem. Soc.* **1959**, *81*, 549.

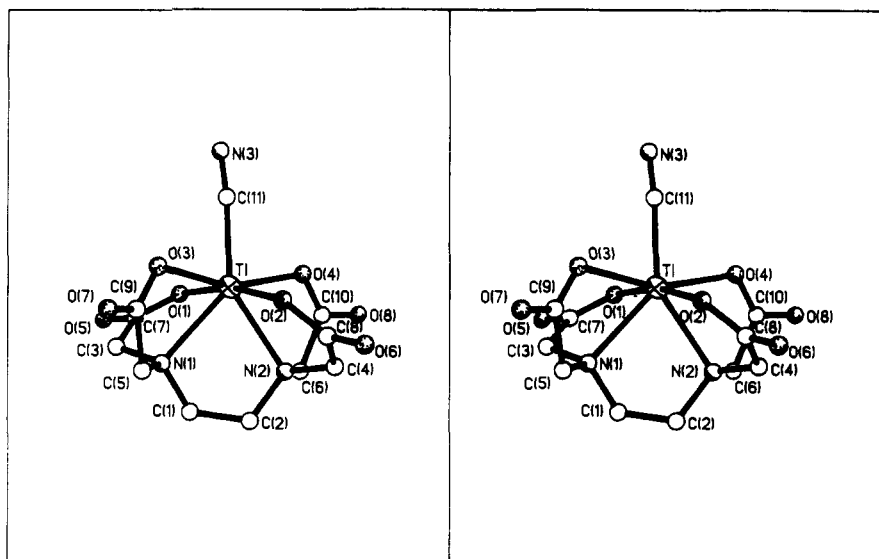
(41) Lind, M. D.; Hamor, M. J.; Hamor, T. A.; Hoard, J. L. *Inorg. Chem.* **1964**, *3*, 34.

(42) Stezowski, J. J.; Countryman, R.; Hoard, J. L. *Inorg. Chem.* **1973**, *12*, 1749.

(43) Fackler, J. P.; Kristine, F. J.; Mazany, A. M.; Moyer, T. J.; Shepherd, R. E. *Inorg. Chem.* **1985**, *24*, 1857.

(44) Richards, S.; Pedersen, B.; Silverton, J. V.; Hoard, J. L. *Inorg. Chem.* **1964**, *3*, 27.





**Figure 8.** Crystal structure of  $\text{Na}_2\text{Tl}(\text{edta})\text{CN}\cdot 3\text{H}_2\text{O}$ . Stereoscopic view of the molecular structure of the complex  $\text{Tl}(\text{edta})\text{CN}^{2-}$  in the solid state. The numbering scheme is indicated. The thermal ellipsoid for Tl includes 50% probability. Bond distances within the coordination sphere of thallium are given in the text.

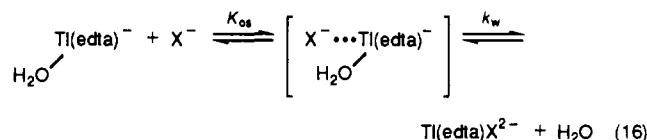
**Table III.** Fractional Atomic Coordinates and Equivalent Isotropic Displacement Coefficients with Estimated Standard Deviations in Parentheses for the Crystal Structure of  $\text{Na}_2\text{Tl}(\text{edta})\text{CN}\cdot 3\text{H}_2\text{O}$  (for the Numbering Scheme, See Figure 8.)

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>equi</sub> (Å <sup>2</sup> )
Tl	0.0931 (1)	0.3039 (1)	0.70850 (5)	0.026 (1)
N1	0.1137 (22)	0.4741 (11)	0.7155 (10)	0.023 (4)
N2	-0.2065 (23)	0.3557 (13)	0.6951 (10)	0.027 (4)
C1	-0.0633 (27)	0.5091 (14)	0.6836 (12)	0.023 (4)
C2	-0.2070 (30)	0.4575 (16)	0.7125 (13)	0.031 (5)
C3	0.2324 (27)	0.5010 (14)	0.6636 (12)	0.024 (4)
C4	-0.2830 (30)	0.3000 (17)	0.7487 (13)	0.034 (5)
C5	0.1807 (28)	0.5019 (16)	0.7986 (12)	0.028 (5)
C6	-0.2907 (30)	0.3351 (16)	0.6101 (13)	0.033 (5)
O1	0.1504 (21)	0.3620 (12)	0.5865 (9)	0.036 (4)
O2	0.0019 (24)	0.2745 (12)	0.8259 (10)	0.044 (4)
O3	0.3399 (20)	0.3563 (11)	0.8098 (9)	0.031 (3)
O4	-0.0982 (21)	0.2022 (12)	0.6234 (10)	0.041 (4)
C7	0.2147 (28)	0.4428 (15)	0.5872 (12)	0.027 (5)
C8	-0.1631 (31)	0.2747 (16)	0.8263 (13)	0.030 (5)
C9	0.3212 (26)	0.4315 (14)	0.8398 (11)	0.023 (4)
C10	-0.2443 (33)	0.2334 (18)	0.5908 (14)	0.038 (6)
Na1	0.4928 (13)	0.2362 (7)	0.4171 (6)	0.039 (2)
Na2	0.3868 (13)	0.0832 (7)	0.5470 (6)	0.043 (2)
O5	0.2705 (23)	0.4806 (12)	0.5321 (10)	0.044 (4)
O6	-0.2275 (27)	0.2537 (15)	0.8847 (12)	0.057 (5)
O7	0.4090 (22)	0.4594 (12)	0.9075 (10)	0.040 (4)
O8	-0.3621 (23)	0.1885 (12)	0.5419 (10)	0.045 (4)
C11	0.2682 (31)	0.1892 (17)	0.7011 (14)	0.035 (5)
N3	0.3688 (32)	0.1331 (17)	0.6886 (14)	0.052 (6)
O9	0.2212 (21)	0.2176 (11)	0.4809 (10)	0.039 (4)
O10	0.4530 (24)	0.1064 (13)	0.9253 (11)	0.050 (5)
O11	0.1727 (29)	0.5509 (16)	1.0249 (13)	0.068 (6)

the comparison to the present structure might not be entirely valid. The drastic increase of this distance from  $\text{Ti}^{4+}$  to  $\text{Fe}^{3+}/\text{Mg}^{2+}$  indicates that the latter are on the verge of being totally encircled by edta (like  $\text{Co}^{3+}$ , see above). For ions larger than  $\text{Ti}^{3+}$ , e.g.  $\text{La}^{3+}$  (ionic radius 1.15 Å) the trend continues:  $\text{La}^{3+}$  is located 0.60 Å above the oxygen plane in  $\text{KLa}(\text{OH}_2)_2(\text{edta})\cdot 5\text{H}_2\text{O}$ , and accordingly, there is enough room for three coordinated water molecules giving a total coordination number of 9.<sup>45</sup>

**Mechanistic Considerations.** Using the rate constants  $k_d$  of the dissociation reaction 13 and the stability constants  $K_X$  (eq 2) for the mixed complexes  $\text{Tl}(\text{edta})\text{Br}^{2-}$  and  $\text{Tl}(\text{edta})\text{SCN}^{2-}$ , the rate constants of the formation reaction can be calculated as

$k_f^X = k_d^X K_X$ . The obtained values,  $k_f^{\text{Br}} = 8.63 (\pm 0.10) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_f^{\text{SCN}} = 1.02 (\pm 0.08) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , are very close to each other. The corresponding values for  $k_f^{\text{Cl}}$  and  $k_f^{\text{CN}}$  could not be measured, but the estimated limits make it possible that also these values fall into the same range. Thus (at least for  $X = \text{Br}$  and  $\text{SCN}$ ) the formation rate of the complexes does not depend on the quality of the entering ligand. Accordingly, assuming that the solid state structure of the complex  $\text{Tl}(\text{edta})\text{X}^{2-}$  persists in solution, we propose that the rate-determining step is the water dissociation ( $k_w$ ) from the intermediate:



In the case of the dissociative mechanism ( $\text{D}$  or  $\text{I}_d$ ), approximately the same activation parameters are expected for the formation reactions involving different  $X$  (see, e.g., eq 13 for  $X = \text{SCN}$ ). Indeed, for the two complexes  $\text{Tl}(\text{edta})\text{Br}^{2-}$  and  $\text{Tl}(\text{edta})\text{SCN}^{2-}$ ,  $\Delta H^\ddagger = 49 (\pm 2)$  and  $47 (\pm 2) \text{ kJ mol}^{-1}$ , and  $\Delta S^\ddagger = -15 (\pm 8)$  and  $-6 (\pm 6) \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. These values are also similar to the activation parameters of the water exchange for  $\text{Tl}_{\text{aq}}^{3+}$  in 3 M  $\text{HClO}_4$ :  $\Delta H^\ddagger = 49 (\pm 2) \text{ kJ mol}^{-1}$ , and  $\Delta S^\ddagger = +12 (\pm 0.3) \text{ J mol}^{-1} \text{ K}^{-1}$ . The estimated rate of water exchange for the hydrated  $\text{Tl}^{3+}$  ion is  $3 \times 10^8 \text{ s}^{-1}$ .<sup>12,13</sup> The corresponding rate constant for  $\text{Tl}(\text{edta})_{\text{aq}}^-$  can be estimated using  $k_f = 9.3 \times 10^6 \text{ M}^{-1}$  as an average of the rate constants for the formation of  $\text{Tl}(\text{edta})\text{Br}^{2-}$  and  $\text{Tl}(\text{edta})\text{SCN}^{2-}$ . Taking into account the outer-sphere repulsion by means of the outer-sphere complex formation constant,  $K_{os} = 0.074 \text{ M}^{-1}$  for two  $-1$  charged ions,<sup>46</sup> we obtain  $k_w = k_f/K_{os} = 1.3 \times 10^8 \text{ s}^{-1}$ . A dissociative mechanism is assumed, with the rate-determining step being water leaving the intermediate. This rate constant is of the same order of magnitude as the corresponding rate constant for  $\text{Tl}_{\text{aq}}^{3+}$ . The exchange rate for one particular water molecule can be calculated, if we take into consideration the number of the bound water molecules in  $\text{Tl}_{\text{aq}}^{3+}$  and  $\text{Tl}(\text{edta})_{\text{aq}}^-$ . The hydration number of  $\text{Tl}^{3+}$  is 6;<sup>47</sup> thus, the water exchange rate for one particular water is  $k_w' = 5 \times 10^7 \text{ s}^{-1}$ . In order to calculate the corresponding constant for  $\text{Tl}(\text{edta})_{\text{aq}}^-$ , we assume one water molecule in this complex, according to eq

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16. Hence,  $k_w' = k_w \sim 1.3 \times 10^8 \text{ s}^{-1}$ , slightly higher than the corresponding constant for  $\text{Tl}_{\text{aq}}^{3+}$ . The increase in the water exchange rate, if significant, can be attributed to the labilization effect of the ligand,  $\text{edta}^{4-}$ . This type of labilization effect has previously been demonstrated for Fe(III) complexes on the basis of activation volumes.<sup>11</sup>

It is interesting to compare our results to the ones for other metal–amino polycarboxylate (MAPC) mixed complexes. Using the T-jump method, the formation of  $\text{Co}(\text{dcta})(\text{CN})^{3-}$  (1,2-diaminocyclohexanetetraacetate = dcta) was found to be *much* faster than expected for the water exchange rate of  $\text{Co}^{2+}$ . The metal ion is seven-coordinated in the mixed complex in contrast to the six-coordinated  $\text{Co}(\text{dcta})^{2-}$ .<sup>48</sup> For europium(III), the corresponding formation rate constant of the mixed complex has been determined via time course of luminescence emission for  $\text{Eu}(\text{dcta})^-$ -imino-diacetate system,<sup>49</sup>  $k_f = 1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . If we use this rate constant to calculate the water exchange rate following the derivation used for the  $\text{Tl}(\text{edta})^-X^-$  system, we obtain  $k_w = k_f/K_{\text{os}} = 1.3 \times 10^9 \text{ s}^{-1}$  ( $K_{\text{os}} = 0.012 \text{ M}^{-1}$ ). This value is close to the water exchange rate for the  $\text{Eu}_{\text{aq}}^{3+}$  ion.<sup>9</sup> It is likely that  $\text{Tl}(\text{edta})_{\text{aq}}^-$  behaves similarly to rare-earth APC complexes, in which some water molecules can also be coordinated to the metal ion.

The values of the second-order rate constant,  $k_2$ , for  $\text{CN}^-$  and  $\text{SCN}^-$  (reactions 14 and 15) are very similar, indicating no dependence on the quality of the entering ligand. If we consider the same intermediate for these reactions as proposed earlier for reaction 16, with the water exchange as the rate-determining step, then the rate constants  $k_1$  and  $k_2$  should lead to the same  $k_w$ . In fact, since  $k_2 \sim 2.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  (average value for reactions 14 and 15) and  $k_{\text{os}} = 0.012 \text{ M}^{-1}$ , we obtain  $k_w = k_2/K_{\text{os}} = 1.9 \times 10^8 \text{ s}^{-1}$ . This value is close to the  $k_w$  value for the reaction 16 (for  $X = \text{SCN}$  and  $\text{Br}$ ), which would support the hypothesis of similar intermediate and rate-determining step for the two reaction types.

A complication arises from the fact that the values of the outer-sphere complex formation constants estimated above are rough and may be quite incorrect, if for example the *real* effective charge of the incoming ligand cannot be approximated to  $-1$ , but rather is lower and perhaps not equal for  $\text{CN}^-$  and  $\text{SCN}^-$ . In fact, according to different calculations the charge of the  $\text{CN}^-$  ion is distributed nearly symmetrically over the carbon and nitrogen atoms,<sup>50</sup> whereas for  $\text{SCN}^-$  most of the negative charge is located on nitrogen and only 0.25  $e^-$  on sulfur.<sup>51</sup> Moreover, both ions are elongated and not spherical, making the calculation of  $K_{\text{os}}$  more uncertain.

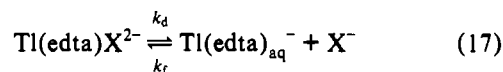
## Conclusions

The  $\text{Tl}(\text{edta})_{\text{aq}}^-$  ion does normally not dissociate in aqueous solution and thus can be treated as a metal ion with one free coordination site. This large ion preserves the complex formation ability of the "parent"  $\text{Tl}_{\text{aq}}^{3+}$  ion in the sense that it forms strong  $\text{Tl}(\text{edta})X^{2-}$  complexes for those ligands  $X^-$  which form strong complexes with  $\text{Tl}^{3+}$ . In fact, for the three ligands for which the stability constants of both  $\text{Tl}(\text{edta})X^{2-}$  and  $\text{TlX}_n^{3-n}$  are known,

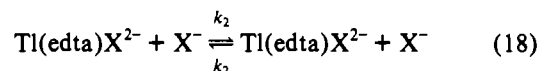
there is a close relationship in their values: 2.3 and 2.8, 3.5 and 4.1, and 8.7 and 7.4, for  $X = \text{Cl}$ ,  $\text{Br}$ , and  $\text{CN}$ , respectively. In addition, the  $\text{Tl}-\text{CN}$  distance in  $\text{Tl}(\text{edta})(\text{CN})^{2-}$  (see above) is close to that in the species  $\text{Tl}(\text{CN})_4^-$  in aqueous solution.<sup>39</sup> The complex  $\text{Tl}(\text{edta})\text{CN}^{2-}$  has the largest stability constant of all known  $\text{Tl}(\text{edta})X^{2-}$  species. This fact is reflected in the extremely large spin–spin coupling,  $^1J(^{205}\text{Tl}-^{13}\text{C}) = 10\,479 \text{ Hz}$ , in the same way as for the previously investigated  $\text{Tl}(\text{CN})_n^{3-n}$  complexes, which in turn are the strongest known monodentate complexes of thallium(III).<sup>14</sup>

As a result of the strength of the  $\text{Tl}-\text{C}$  bond the  $\text{Tl}(\text{edta})(\text{CN})^{2-}$  complex is very stable, and the kinetics for the cyanide system differs from the behavior of the other studied complexes,  $\text{Tl}(\text{edta})X^{2-}$ . Whereas for  $X = \text{Cl}$ ,  $\text{Br}$ , and  $\text{SCN}$  the dissociation reaction 12 ( $k_d$ ) is relatively fast on the actual time scale, for  $X = \text{CN}$  it is so slow that it does not influence the line widths of the actual NMR spectra.

We propose a dissociative mechanism for the first of the two dominating pathways of  $X$  ligand exchange in the  $\text{Tl}(\text{edta})^-X^-$  systems, namely

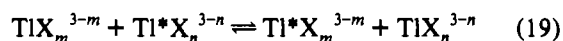


The rate-determining step is the water dissociation from the intermediate ( $k_w$ , eq 16). Also for the other dominating exchange reaction



a reaction mechanism can be proposed which includes water dissociation as a rate-determining step. A comparison of water dissociation rates estimated for the  $\text{Tl}_{\text{aq}}^{3+}$  ion and for  $\text{Tl}(\text{edta})X^{2-}$  indicates that the water molecule in the latter compound is labilized, possibly due to the higher coordination number of thallium.

Recently, we proposed a similar mechanism for the reaction



where  $X = \text{Cl}^{12}$  and  $\text{Br}$ .<sup>13</sup> Interestingly, if the assumptions inherent in the calculation of stability constant for the outer-phase complex ( $K_{\text{os}}$ ) are approximately correct, the dissociation rates of one particular water molecule are similar for  $\text{Tl}(\text{edta})X^{2-}$  and  $\text{TlX}_n^{3-n}$ .

Reaction 19, which dominates the halide exchange for  $\text{TlCl}_n^{3-n}$  and  $\text{TlBr}_n^{3-n}$  in a wide  $X/\text{Tl}$  range,<sup>12,13</sup> is apparently not important for  $\text{Tl}(\text{edta})X^{2-}$ . It is possible that the large  $\text{Tl}(\text{edta})X^{2-}$  ion is not likely to approach another  $\text{Tl}(\text{edta})X^{2-}$  or  $\text{Tl}(\text{edta})^-$  so that a suitable geometric configuration leading to an exchange of  $X^-$  can occur.

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**Supplementary Material Available:** Listings of crystal data, data collection and structure refinement parameters, atomic coordinates and thermal parameters, and bond distances and angles and a figure showing the  $^1\text{H-NMR}$  spectra of  $\text{Tl}(\text{edta})^-$  complex in  $\text{D}_2\text{O}$  (experimental and simulated) (8 pages). Ordering information is given on any current masthead page.

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