

# Mixed-Ligand Chelate Complexes of Thallium(III), Characterized by Equilibrium Measurements, NMR and Raman Spectroscopy, and X-ray Crystallography

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Equilibria in aqueous solutions at ionic strength  $I = 1.00$  (NaClO<sub>4</sub> or NaNO<sub>3</sub>) and 25 °C between the 1:1 thallium(III) complexes [Tl(L)] (L are diaminotetraacetate ligands edta and cdta and the hexaamine tpen {tetrakis(2-pyridylmethyl)ethylenediamine}) and different coligands A (A are OH<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, SCN<sup>-</sup>, N<sub>3</sub><sup>-</sup>, py, en, Hen<sup>+</sup>, phen, bpy, gly<sup>-</sup>, Hgly, ox<sup>2-</sup>, and ida<sup>2-</sup>) have been investigated by means of potentiometric pH titrations and <sup>13</sup>C and <sup>1</sup>H NMR, Raman, and IR spectroscopy. Each ligand gives rise to the following equilibria, allowing the determination of the corresponding equilibrium constants by pH measurements: (1) [Tl(L)(H<sub>2</sub>O)]<sup>n</sup> ⇌ [Tl(L)(OH)]<sup>n-1</sup> + H<sup>+</sup>; (2) [Tl(L)(H<sub>2</sub>O)]<sup>n</sup> + A ⇌ [Tl(L)(A)]<sup>n</sup> + H<sub>2</sub>O. The presence of [Tl(L)(A)] in solution and the corresponding data have been confirmed by NMR for [Tl(edta)(A)] and [Tl(cdta)(A)]: Although the <sup>13</sup>C coordination chemical shifts are small, heteronuclear coupling constants  $J(^{205/203}\text{Tl}, ^{13}\text{C})$  and, in particular, those involving the carboxylate function can be employed for monitoring structural changes and the determination of equilibrium constants. The cdta complexes, having a rigid stereochemistry imposed by the cyclohexyl ring, in solution exhibit conformations for the glycine-type chelate rings which are close to those found in the solid for analogous edta complexes. The parameter <sup>3</sup>J(Tl,H) for the acetate groups of the cdta ligand established conformational similarities for all the complexes with monodentate coligands A, different from those coordinating in a bidentate fashion, suggesting that also the complex [Tl(L)(H<sub>2</sub>O)]<sup>n</sup> exists as a monoquo species, i.e.,  $n = 1$ . Two-dimensional NMR for [Tl(cdta)(phenH)] and [Tl(cdta)(phen)]<sup>-</sup> provides simple and direct evidence for the formation of stable mixed-ligand complexes with CN = 7 and 8 in aqueous solution. Raman spectra of solutions with equilibria of types (1) and (2) for L = edta allow the assignment of bands to the mixed-ligand complexes present in agreement with the equilibrium constants obtained. The X-ray crystal structures of two complexes which were isolated in crystalline form, i.e., Ca[Tl(edta)(OH)]·3H<sub>2</sub>O (monoclinic, space group  $P2_1/c$ ,  $a = 13.744(8)$  Å,  $b = 9.141(2)$  Å,  $c = 13.752(0)$  Å,  $\beta = 100.71(0)^\circ$ ,  $Z = 4$ ) and [Tl(tpen)(NO<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub> (monoclinic, space group  $P2_1/c$ ,  $a = 12.718(6)$  Å,  $b = 13.640(7)$  Å,  $c = 18.883(9)$  Å,  $\beta = 108.84(4)^\circ$ ,  $Z = 4$ ) showed a CNs of 7 for the former and 8 for the latter Tl(III) complex salt.

## Introduction

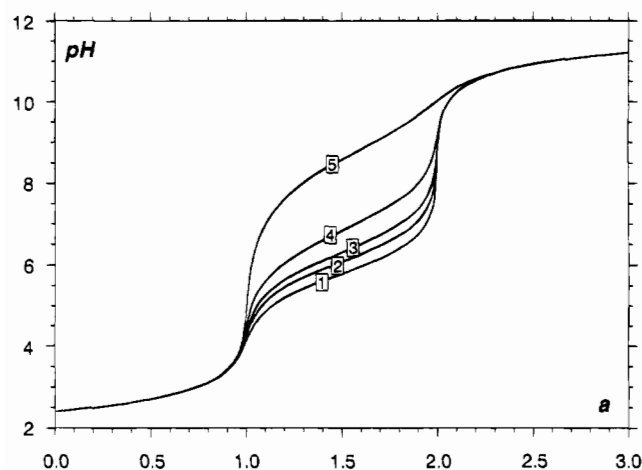
1:1 complexes ML in which the chelating ligand L is not able to fully enclose the central ion can have some sites available for the coordination of a second ligand A, thus allowing for the formation of mixed-ligand complexes MLA. Complexes of this kind are quite common when the individual ligands L and A contain from one to three available donor atoms but are much less frequent when L has at least six such atoms. Indeed the coordination number (CN) of metal ions is often 6, and thus in the 1:1 complexes there is no additional site free for further coordination. This is the case for edta complexing 3d two- and three-valent metal ions where, in the solid state, only Mn<sup>2+</sup> and Fe<sup>2+</sup> have been shown to contain a coordinated water molecule,<sup>2,3</sup> forming the 7-coordinated mixed-ligand complex ions [M(L)(H<sub>2</sub>O)]. As shown by Martell and co-workers,<sup>4,5</sup> when metal ions preferring larger CNs are used, it is possible to obtain

mixed-ligand complexes, e.g., starting from the 1:1 Th<sup>IV</sup>- and U<sup>IV</sup>edta complexes with, e.g., pyrocatechol derivatives or iminodiacetate. Also the lanthanide(III) cations, favoring CNs up to 9 and 10, easily form mixed-ligand complexes with edta and *o*-hydroxyquinoline-5-sulfonate, as well as with iminodiacetate (ida) and nitrilotriacetate (nta).<sup>6</sup> A particular case is the edta complexes of Cu(II), Ni(II), and Co(II) exhibiting spectral changes in the presence of large concentrations of ammonia, hydroxylamine, hydrazine, and pyridine,<sup>7</sup> presumably due to the substitution of one of the coordinated carboxylate groups with one of these additional ligands, without an increase of the CN of the metal ions. Among the 1:1 edta complexes which are considered to be predestined to give mixed-ligand complexes are those showing coordinated H<sub>2</sub>O molecules, as they could contain central ions with CN > 6. Tl<sup>3+</sup> belongs to this category as demonstrated by the fact that [Tl(edta)(H<sub>2</sub>O)]<sup>-</sup> is a weak acid forming [Tl(edta)(OH)]<sup>2-</sup>.<sup>8</sup> In these complexes the coordinated H<sub>2</sub>O or OH<sup>-</sup> can also be substituted by other monodentate ligands such as halides<sup>9-11</sup> or pseudohalides<sup>11,12</sup> or neutral ligands such as ethylenediamine.<sup>12</sup> The investigation of thallium(III) complexes with two other hexadentate ligands,

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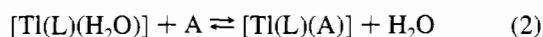
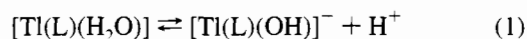
**Figure 1.** Alkalimetric titration curves, pH vs *a* (neutralization parameter), for H[Tl(edta)(H<sub>2</sub>O)], 4 mM, *I* = 1.00 M (NaClO<sub>4</sub>) (1), and in the presence of coligands X = Cl (2), SCN (3), Br (4), and I (5).

namely *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetate (cdta) and the polyamine tetrakis(2-pyridylmethyl)ethylenediamine (tpen),<sup>13</sup> has shown very similar behaviors of their 1:1 complexes as monoprotic acids and also very similar magnitudes for the corresponding *pK* values.

We report here the behavior of the 1:1 Tl(III) complexes with the three hexadentate ligands in the presence of coligands leading to the formation of mixed-ligand complexes. Our equilibrium studies have been corroborated by the crystal structures of Ca[Tl(edta)(OH)] and [Tl(tpen)(NO<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub>, showing that CNs of 7 and 8, respectively, are possible in these Tl(III) complexes. This conclusion has been confirmed by NMR, IR, and Raman spectroscopic studies of these and related species in solution.

## Results and Discussion

**A. Equilibrium Studies.** The three complexes [Tl(L)(H<sub>2</sub>O)] (L = edta, cdta, and tpen) in solution between pH 5 and 7 behave as weak monoprotic acids, liberating a proton H<sup>+</sup>, according to eq 1. The resulting species are stable in the



presence of an excess of strong base. If the solution contains also a second complexing agent A, both equilibria 1 and 2 have to be considered and the concentrations of the various thallium species depend on the magnitude of the equilibrium constant of eq 2,  $K = [\text{Tl}(\text{L})(\text{A})]/([\text{Tl}(\text{L})(\text{H}_2\text{O})][\text{A}]$  and on the concentration of free A. In general, this implies a decrease in the concentration of [Tl(L)(H<sub>2</sub>O)] with a corresponding displacement of the buffer range due to (1) toward higher pH values. This is depicted in Figure 1, which shows some alkalimetric titration curves, pH vs *a* (the neutralization parameter, defined as [OH<sup>-</sup>]/[H[Tl(edta)(H<sub>2</sub>O)]], where [OH<sup>-</sup>] is the total concentration of the added strong base), for the strong acid H[Tl(edta)-

**Table 1.** Protonation Constants of the Ligands A<sup>a</sup>

ligand		<i>pK</i>	
		<i>I</i> <sup>b</sup> = 1.00 (NaClO <sub>4</sub> )	<i>I</i> = 1.00 (NaNO <sub>3</sub> )
azide	N <sub>3</sub> <sup>-</sup>	4.43	4.44
1,10-phenanthroline	phen		5.18
2,2'-bipyridine	bipy	4.93	4.72
ethylenediamine	en	10.14	10.05
	Hen <sup>+</sup>	7.47	7.44
glycinate	gly <sup>-</sup>	9.60	9.61
	Hgly	2.46	2.30
iminodiacetate	ida <sup>2-</sup>		9.16
	Hida <sup>-</sup>		2.65

<sup>a</sup> Measured at 25 °C. <sup>b</sup> Ionic strength.

**Table 2.** Logarithm of Stability Constants of the Mixed-Ligand Complexes [Tl(L)(A)]<sup>a</sup>

A	L		
	edta <sup>b</sup>	cdta <sup>c</sup>	tpen <sup>c</sup>
OH <sup>-</sup>	7.90(5)	7.20(5)	8.40(5)
Cl <sup>-</sup>	2.52(10)	1.86(10)	3.56(5)
Br <sup>-</sup>	3.70(5)	2.80(10)	4.17(5)
I <sup>-</sup>	5.47(10)	4.79(5)	5.56(5)
SCN <sup>-</sup>	2.94(10)	2.21(10)	2.76(10)
N <sub>3</sub> <sup>-</sup>	3.56(5)	3.28(5)	4.33(5)
py	2.58(10)		
en	8.65(10)	7.68(10)	
Hen <sup>+</sup>	5.49(20)	5.87(20)	
phen	4.75(5)	3.64(5)	2.34(10)
Hphen <sup>+</sup>		2.77(7)	
bipy	3.21(10)	2.20(10)	
gly <sup>-</sup>	5.9(2)		
Hgly	5.2(3)		
ox <sup>2-</sup>	2.62(20)	2.10(20)	2.9(1)
ida <sup>2-</sup>	4.72(20)		

<sup>a</sup>  $K = [\text{Tl}(\text{L})(\text{A})]/([\text{Tl}(\text{L})][\text{A}]$  at *I* = 1.00 M and 25 °C. The values given in parentheses are 3 times the standard deviation. <sup>b</sup> *I* = 1.00 (NaClO<sub>4</sub>). <sup>c</sup> *I* = 1.00 (NaNO<sub>3</sub>).

(H<sub>2</sub>O)], ionic strength *I* = 1.00 (NaClO<sub>4</sub>), in the presence of sodium halides and thiocyanate. H[Tl(edta)(H<sub>2</sub>O)] is a two-protonic acid, and in the presence of a ligand A is involved in equilibria 1 and 2. The formation of the mixed-ligand complex [Tl(edta)(A)] occurs predominantly in the range *a* = 0 to *a* = 1, where the strong acid is neutralized. Further addition of base is accompanied by the formation of [Tl(edta)(OH)]<sup>2-</sup>, but this reaction occurs at different pH values, depending on the constant *K* of eq 2. Its increase is accompanied by a decrease in the concentration of [Tl(edta)(H<sub>2</sub>O)]<sup>-</sup>, thus resulting in higher pH values. This can be seen by comparison of the values for *K* in Table 2 and the corresponding curves in Figure 1. Among the anions studied, I<sup>-</sup> forms the most stable mixed-ligand complexes and its exchange with OH<sup>-</sup> occurs only above pH 7, whereas Cl<sup>-</sup> is practically fully substituted at the same pH value. The description of such equilibria is straightforward as long as the ligand A itself is not involved in a protonation equilibrium. In this latter case, the concentration of the protonated species HA has also to be considered. The formation of mixed-ligand complexes from HA is accompanied by a pH decrease. Furthermore, the formation of protonated mixed-ligand complexes of the type [Tl(L)(HA)] could occur. After *a* = 2, the curves collapse again as expected. It should be noted that OH<sup>-</sup> consumption is not observed in this pH range for fresh solutions; aging, however, results in a decrease in the pH values presumably due to decomposition.

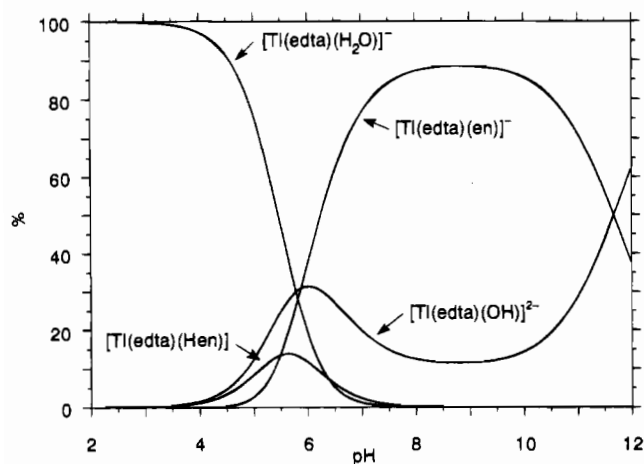
The obtained equilibrium constants are summarized in Tables 1 and 2 for HA and the mixed-ligand complexes [M(L)(A)], respectively. Because of the different basicities of the ligands A employed, values of the constants *K* of the same magnitude

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**Figure 2.** Species distribution as a function of pH for the  $[\text{Tl}(\text{edta})(\text{H}_2\text{O})]^-/\text{ethylenediamine}$  system.

do not imply the formation of the same concentration of the mixed-ligand complex in solution. Thus in the case of 1,10-phenanthroline (phen), having a  $\text{p}K$  for  $\text{Hphen}^+$  of 5.18 and a  $\log K$  of 4.75, the mixed-ligand complex represents up to 90% of  $[\text{M}(\text{L})]_{\text{total}}$  for millimolar solutions of the reagents, whereas the concentration of  $[\text{Tl}(\text{L})(\text{A})]$  for  $\text{A} = \text{iminodiacetate} (\text{ida})$ , with a  $\text{p}K$  for  $\text{Hida}^-$  of 9.16 and  $\log K$  of 4.72, is 10 times lower. This arises because, under the conditions in which the complex  $[\text{Tl}(\text{L})(\text{H}_2\text{O})]$  is present in solution, iminodiacetate is always protonated but 1,10-phenanthroline not. As a consequence, the error of the constant is much larger for ida than for phen.

The reliability of the constants obtained was checked by simulation of the titration curves employing  $K$  as well as the other equilibrium constants involved and further controlled by comparing the experimental with the calculated curves in the case where no mixed-ligand complex is expected to be formed. In the case of ida, the pH difference between these two computed curves is close to the experimental error of ca.  $\pm 0.02$ , in spite of the large value of  $K$ . The large standard deviation of  $K$  in the case of  $\text{SCN}^-$  and  $\text{I}^-$  is due to slow partial reduction of the Tl(III) complex. Figure 2 shows the species distribution in the case of the coligand ethylenediamine (en) for solutions with equimolar amounts (4 mM) of  $[\text{Tl}(\text{edta})]^-$  and en. At lower pH values, a protonated mixed-ligand complex  $[\text{Tl}(\text{L})(\text{enH})]$  is observed and a pH increase leads to the complex  $[\text{Tl}(\text{L})(\text{en})]^-$ , while the formation of the hydroxo species is largely suppressed. From the pH measurements it cannot be established where protonation occurs, and an alternative formulation for  $[\text{Tl}(\text{L})(\text{HA})]$  would be  $[\text{Tl}(\text{HL})(\text{A})]$  where A shows bidentate coordination and one of the arms of L is protonated. This possibility, however, can be ruled out from the NMR measurements, which clearly established that all carboxylates are coordinated and that dynamic processes involving these groups are absent.

The constants  $K$  for the mixed-ligand complexes formed by  $[\text{Tl}(\text{edta})(\text{H}_2\text{O})]^-$  with the monodentate ligands  $\text{CN}^-$  ( $\log K = 8.72 \pm 0.09$ ),  $\text{SCN}^-$  ( $\log K = 2.79 \pm 0.09$ ), and  $\text{Cl}^-$  ( $\log K = 2.6 \pm 0.2$ ), obtained by NMR spectroscopy, were published recently.<sup>11</sup> The values for the ligands in common, i.e.,  $\text{OH}^-$ ,  $\text{Cl}^-$ , and  $\text{SCN}^-$ , agree well with ours. There is also agreement with previously determined constants for  $\text{Br}^-$  and  $\text{Cl}^-$ .<sup>10</sup>

From Figures 1 and 2 it appears that down to pH 2 no protonation of  $[\text{Tl}(\text{edta})(\text{H}_2\text{O})]^-$  occurs, as expected if no uncomplexed donor group is present in the above complex. The same is true for the 1:1 complexes with cdta and tpen and is a hint that the complexes  $[\text{Tl}(\text{L})(\text{H}_2\text{O})]$  in water contain thallium-

(III) bound to six donor atoms of the ligand L and one  $\text{H}_2\text{O}$  molecule.

The use of different electrolytes and the significance of the constants thus obtained merit a comment: The use of different inert salts in the investigation of ionic equilibria is sometimes unavoidable due to the insolubility of some of the species, which entirely precludes the measurements. It appears from the results shown in Table 1 that the  $\text{p}K$  values measured by the use of different inert salts at the same ionic strength differ more than expected. There is, however, a dependence on the activity coefficients  $\gamma_{\pm}$  of the involved salts which are indeed different, i.e., 0.629 and 0.548 in 1 *m* solutions at 25 °C for  $\text{NaClO}_4$  and  $\text{NaNO}_3$ , respectively.<sup>14</sup> Differences in the  $\text{p}K$  values are, therefore, expected, even without considering the occurrence of ion pairs and complex formation with the species involved in the equilibrium, which would both further alter the values of the equilibrium constant. In the literature one finds for, e.g., bipy<sup>15</sup> the same difference  $\text{p}K(\text{NaClO}_4) - \text{p}K(\text{NaNO}_3) = 0.21$  as in our data, whereby the parameter in both cases is 0.04 lower. The mean values for each medium should be considered as more representative.

The stability constant of, e.g., the edta complex of  $\text{Tl}^{3+}$  is generally expressed in the form of  $K = [\text{Tl}(\text{edta})]/([\text{Tl}][\text{edta}]$ ,<sup>16</sup> neglecting the contributions of the remaining species present in solution. For  $\text{Tl}^{3+}$  a high ionic strength is necessary as this cation is only stable in the presence of 1 M strong acid. With respect to the use of inert electrolytes, it can be stated that  $\text{KNO}_3$  is generally preferred to  $\text{NaClO}_4$  and  $\text{KCl}$  because (i)  $\text{Na}^+$  forms stronger edta complexes than  $\text{K}^+$  and (ii)  $\text{Cl}^-$  is expected to form more stable metal complexes than  $\text{NO}_3^-$ . For the  $\text{Tl}^{3+}$  ion, complexation by  $\text{NO}_3^-$  is, however, expected.<sup>17</sup> Also the eventual formation of ion pairs should in principle be considered. All these factors are influencing the effective concentrations of  $\text{Tl}^{3+}$ ,  $\text{edta}^{4-}$ , and  $[\text{Tl}(\text{edta})]^-$ , and these are thus lower than (or equal to) the concentrations which are used to calculate  $K$  in the above expression. From this point of view the expression for  $K$  is approximative at its best and any choice of a particular inert electrolyte is normally inappropriate.

**B. NMR Spectroscopy.** One- and two-dimensional nuclear magnetic resonance measurements were performed with respect to (i) confirming the formation of mixed-ligand complexes  $[\text{Tl}(\text{L})(\text{A})]$  as was indicated by the before-mentioned equilibrium measurements, (ii) establishing their solution structures, which in this context not only means the determination of the coordination number but also includes aspects of configuration and conformation, and (iii) assessing qualitatively their behavior with respect to ligand exchange, i.e. their kinetic properties. While the use of either  $^{13}\text{C}$ <sup>11,18</sup> or, in particular,  $^{205}\text{Tl}$ <sup>11</sup> NMR spectroscopy has already proven to be a source of invaluable information in this field of chemistry, so far  $^1\text{H}$  NMR methods are less frequently encountered.

**Complexes with Coordination Number 7.**  $^{13}\text{C}$  and  $^1\text{H}$  NMR data were recorded for the complexes  $[\text{Tl}(\text{L})(\text{A})]$  ( $\text{L} = \text{edta}$  and  $\text{cdta}$ ;  $\text{A} = \text{H}_2\text{O}$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{SCN}^-$  and  $\text{CN}^-$ ) and are summarized in supplementary Tables S1 and S2. It had previously been mentioned<sup>18</sup> that  $^{13}\text{C}$  coordination chemical

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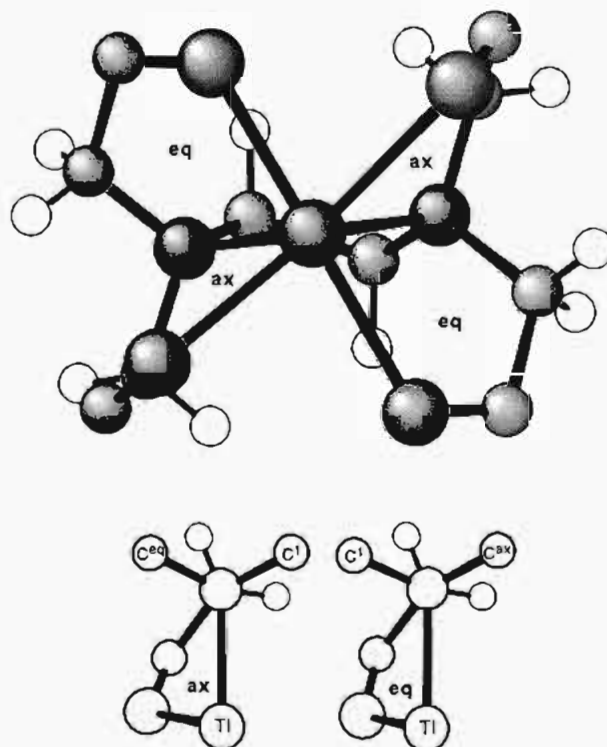
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shifts ( $=\delta(\text{complex}) - \delta(\text{ligand})$ ) are disappointingly small for the system  $[\text{Tl}(\text{edta})]^-$  and therefore of very limited diagnostic value. This finding can be fully confirmed by the data obtained in this study covering an extended set of thallium edta and cdta complexes containing a large variety of anionic, neutral, and cationic coligands. However, it should be noted that the heteronuclear coupling constants  ${}^nJ(^{205/203}\text{Tl},^{13}\text{C})$ , in particular those involving the carboxylate function, exhibit a larger variation reflecting electronic and/or structural changes occurring in the coordination sphere of the thallium atom. In view of this larger spread and the high precision with which these values can be obtained, such parameters can be employed for monitoring structural changes and determining equilibrium constants. Thus, the stability constant for, e.g.,  $[\text{Tl}(\text{edta}(\text{Cl}))]^{2-}$ , being in fast exchange with  $[\text{Tl}(\text{edta}(\text{H}_2\text{O}))]^-$  on the NMR time scale, can be computed from titration curves obtained by monitoring the changes in  ${}^2J(\text{Tl},\text{COO})_{\text{obsv}} = p \times {}^2J(\text{Tl},\text{COO})_{[\text{Tl}(\text{edta})(\text{H}_2\text{O})]} + (1 - p) \times {}^2J(\text{Tl},\text{COO})_{[\text{Tl}(\text{edta})(\text{Cl})]}$  as a function of added chloride. The use of such NMR parameters requires, however, their unambiguous assignment, and we will discuss this for the example of the aqua/hydroxo complexes.

**Resonance Assignments and Solution Structures of  $[\text{Tl}(\text{cdta})(\text{H}_2\text{O})]^-$  and  $[\text{Tl}(\text{cdta})(\text{OH})]^{2-}$ .** The complexes with the cdta ligand, having a lower symmetry and a rigid conformation imposed by the presence of the cyclohexyl ring, provide a higher degree of information than their edta analogs. In the latter compounds, dynamic averaging of different ligand conformations occurs, thus masking some of the important structural features. We, therefore, start the discussion with the solution characteristics of the complex  $[\text{Tl}(\text{cdta})(\text{H}_2\text{O})]^-$ , mentioning on the way some possible pitfalls in the interpretation of its NMR spectra and showing methods for correct assignments.

The cyclohexyl moiety present in the cdta ligand fixes the conformation of the diamine chelate as shown in the Figure 3. A consequence of this particular ring conformation is that there are two different acetate moieties, which can be described as being either pseudoaxial or pseudoequatorial with respect to this diamine chelate.

The  ${}^1\text{H}$  and  ${}^{13}\text{C}$  resonances of the carbons having hydrogens attached are best assigned from a  ${}^{13}\text{C}-{}^1\text{H}$  heteronuclear correlation. Part of such a spectrum is given in Figure 4A, showing the assignments for the two different acetate fragments. Each of these two groups carries two diastereotopic hydrogens, which turn out to be remarkably different with respect to their thallium couplings; see Table 3. This parameter measures 719 and 6 Hz for the hydrogens in the first and 576 and 61 Hz for those of the second acetate group. Assuming that a Karplus-like relationship<sup>19</sup> is also valid for this kind of vicinal coupling between thallium and protons, the two small coupling constants are interpreted as resulting from a ca.  $85-90^\circ$  torsional angle, where a minimum in the Karplus function is expected. The larger values (719 and 576 Hz), being slightly larger than the 453 Hz observed<sup>20</sup> in the more rigid system  $[\text{Tl}(\text{taci})_2]^{3+}$  (taci = 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol), would then arise from angles of approximately  $160^\circ$ . This clearly points to a well-defined conformation of the glycine-type chelate rings, and it is interesting to note that in the solid state structures of  $[\text{Tl}(\text{edta})(\text{X})]^{2-}$ , X = CN<sup>11</sup> and OH, as determined by X-ray crystallography, dihedral angles of  $158$  and  $80^\circ$  (average) are found, which are close to those deduced here for the solution structure of  $[\text{Tl}(\text{cdta})(\text{H}_2\text{O})]^-$  and for related complexes. Ac-



**Figure 3.** Model for the solution structures of the complexes  $[\text{Tl}(\text{cdta})(\text{A})]^-$  built from the X-ray structures of  $[\text{Tl}(\text{edta})(\text{CN})]^{2-}$  and  $[\text{Tl}(\text{edta})(\text{OH})]^{2-}$  (ligands A, C=O oxygens, and part of the cyclohexyl ring omitted for clarity) showing the pseudoaxial and pseudoequatorial arrangement of the glycine type chelates (top) and conformation determining dihedral angles within these (bottom).

cordingly, we employ these X-ray structures as models for further assignments and discussion of the solution characteristics of the 7-coordinated compounds.

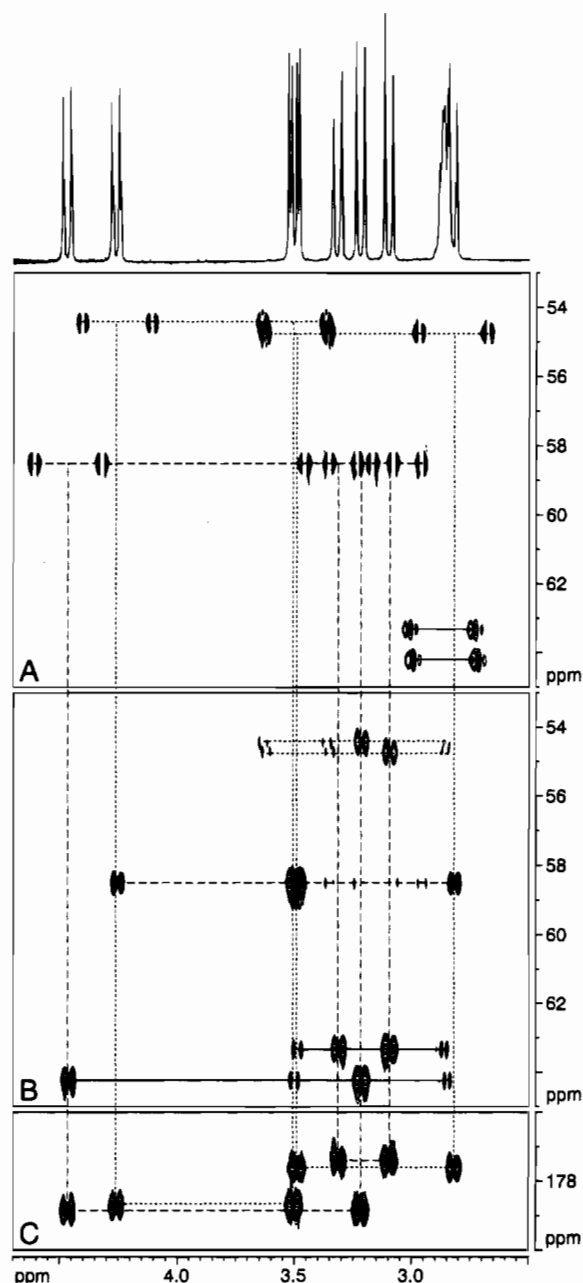
The further assignment of the two types of acetate to the axial and equatorial positions, respectively, follows from the  ${}^{13}\text{C}-{}^1\text{H}$  long-range correlation experiment (Figure 4B). The C(1) carbon of the cyclohexyl group (en part) couples predominantly to two protons of one acetate moiety and weakly to only one hydrogen of the other. On the basis of the above-mentioned models and the known dependence of  ${}^3J(\text{C},\text{H})$  upon torsional angles,<sup>21</sup> stronger crosspeaks are expected for the  $\text{CH}_2$  of the equatorial acetates. Further, the methylene carbon of this equatorial group should show strong coupling to both of the axial  $\text{CH}_2$  protons (relevant dihedral angles are ca.  $40$  and  $160^\circ$ , respectively) whereas, for the other coupling pathway between the axial  $\text{CH}_2$  carbon and the equatorial  $\text{CH}_2$  protons, one of the correlations is expected to be missing (because one of the dihedral angles measures ca.  $80^\circ$ ). Consequently, the carbons resonating at 58.35 and 54.44 ppm are assigned to the pseudoequatorial and pseudoaxial positions, respectively.

The assignment of the respective carboxylate resonances follows from the same type of experiment (see Figure 4C). From the conventional  ${}^{13}\text{C}$  NMR spectrum which shows four lines, as expected, in the appropriate region of the spectrum, it is not immediately obvious which belong together in terms of being the doublet components arising from heteronuclear coupling to the Tl spins. The possibility of two rather different chemical shifts and small heteronuclear coupling constants  $J(\text{Tl},\text{COO})$  of 19 and 28 Hz can be excluded, given the value for the edta complex (143 Hz) and measurements at two different  $B_0$  field strengths. From the two remaining possibilities, one might be

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**Figure 4.** Sections of  $^{13}\text{C}-^1\text{H}$  heteronuclear correlation spectra (11.4 T,  $\text{D}_2\text{O}$ , pD 2, room temperature, no  $^{13}\text{C}$  decoupling) for  $[\text{Tl}(\text{cdta})(\text{D}_2\text{O})]^-$  showing (A) one-bond correlations for the acetate  $\text{CH}_2$  and the en  $\text{C}(1)\text{H}$  entities, (B) long-range interactions for the same groups, and (C) long-range correlations for the carboxylate functions. The pseudoaxial and pseudo-equatorial acetates are indicated by dotted and dashed lines, respectively.

**Table 3.** Vicinal Coupling Constants  $^3J(\text{Tl},\text{H})$  Involving the Acetate Groups in  $[\text{Tl}(\text{cdta})(\text{A})]$  Complexes

A	CN	pH	$^3J(\text{Tl},\text{H}), \text{OAc}^{\text{ax}}, \text{Hz}$	$^3J(\text{Tl},\text{H}), \text{OAc}^{\text{eq}}, \text{Hz}$
$\text{H}_2\text{O}$	7	2	719	61
$\text{OH}^-$	7	11	684	40
$\text{Cl}^-$	7	2	719	21
$\text{CN}^-$	7	10	686	32
phenH	7	5	756	28
phen	8	5	516	310

inclined toward the "symmetrical solution" (155 and 164 Hz), which, however, proved wrong in view of the experiment shown in Figure 4C. Indeed, the actual coupling constants measure 183 and 136 Hz for the equatorial and axial carboxylates, respectively, the  $^{13}\text{C}$  chemical shifts being virtually identical.

The stereochemically sensitive parameters  $^3J(\text{Tl},\text{H})$  are virtually unchanged when  $\text{H}_2\text{O}$  is replaced by other monodentate ligands such as  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , phenH $^+$ , or  $\text{CN}^-$ ; see Table 3. This points to a common conformation of the cdta ligand in these complexes. Furthermore, there are no significant spectral changes when the concentration of the coligands A is increased, as e.g. for  $\text{Br}^-$ ; it is, therefore, suggested that all of these  $[\text{Tl}(\text{cdta})(\text{A})]$  complexes share a common coordination polyhedron with a coordination number equal to 7. Consequently, it is proposed that the solution structures of these complexes are essentially equivalent to those found in the solid state for the analogous edta complexes  $[\text{Tl}(\text{edta})(\text{A})]$ , A =  $\text{CN}^-$  and  $\text{OH}^-$ ; i.e., A is capping the  $\text{O}_4$  face of a distorted trigonal prism formed by the cdta ligand. Furthermore, the similarity of the data for the aquo complex to those of the other monodentate coligands suggests that only one water is coordinated.

In solution the edta complexes have to be considered as being stereochemically nonrigid, resulting in averaging of the pseudo-equatorial and pseudoaxial positions at the en chelate ring, so that only one type of acetate is detected. Additionally, only averaged vicinal coupling parameters  $^3J(\text{Tl},\text{H})$  can be observed for these systems; e.g., for  $[\text{Tl}(\text{edta})(\text{H}_2\text{O})]^-$  these are 372 and 289 Hz.<sup>22</sup>

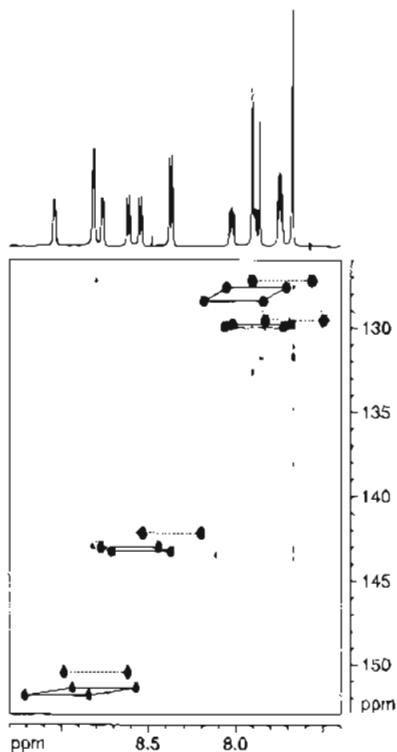
Having clarified the structural features of the species present in solution, we are now able to comment on the observed changes in the coupling constants  $J(\text{Tl},\text{COO})$ , which vary from 181 to 54 Hz in the  $\text{H}_2\text{O}$  and  $\text{CN}^-$  derivatives. The magnitude of this parameter changes as a function of (a) the stereochemical orientation of the acetate, larger values being generally observed for the pseudo-equatorial chelates, and (b) the nature of the coligand A. Changes of the latter parameter cause a decrease in the coupling constants  $J(\text{Tl},\text{C})$  in the order  $\text{H}_2\text{O}$  (181/138 Hz) >  $\text{OH}^-$  (134/88 Hz)  $\approx$   $\text{Cl}^-$  (136/81) >  $\text{Br}^-$  (115/61 Hz) >  $\text{SCN}^-$  >  $\text{CN}^-$  (126/54 Hz). This order parallels the  $\sigma$ -donor capacities of the ligands; therefore, these changes are best assigned to electronic effects.

**Complexes with Coordination Number 8.**  $^{13}\text{C}$  and  $^1\text{H}$  NMR data were recorded for a number of complexes of the type  $[\text{Tl}(\text{L})(\text{A})]$  (L = edta; A = phen, bipy, gly, en, ox; L = cdta; A = phen). Relevant NMR data are summarized in supplementary Tables S3 and S4. Coordination of these bidentate ligands is indicated by significantly decreased values for the couplings between Tl and the carboxylate carbons, e.g.  $[\text{Tl}(\text{edta})(\text{A})]$ , A = phen (92 Hz), bipy (91 Hz), gly (92 Hz), en (85 Hz), ox (119 Hz), compared to  $\text{H}_2\text{O}$  (143 Hz), irrespective of whether the resulting 8-coordinate complexes are dynamic on the NMR time scale or not. Nonrigid behavior has been observed for the coligands bipy, gly, and en, whereas the phen derivatives are robust.

**Solution Structure of  $[\text{Tl}(\text{cdta})(\text{phen})]^-$ .** The phenanthroline complexes have been considered as prototypes in this series and have been investigated more thoroughly also by two-dimensional NMR methods. Although the stability constant for the complex  $[\text{Tl}(\text{cdta})(\text{phen})]^-$  is 1 order of magnitude lower than that for the corresponding edta analog, we begin again the discussion with this complex because of its conformational rigidity.

In aqueous solution at pH  $\approx$  5–6,  $[\text{Tl}(\text{cdta})(\text{phen})]^-$  is present in equilibrium with a second complex formulated as  $[\text{Tl}(\text{cdta})(\text{phenH})]$ . Ligand exchange in the former and between the two species, however, is slow on the NMR time scale, so that both compounds can be observed separately. As judged from the

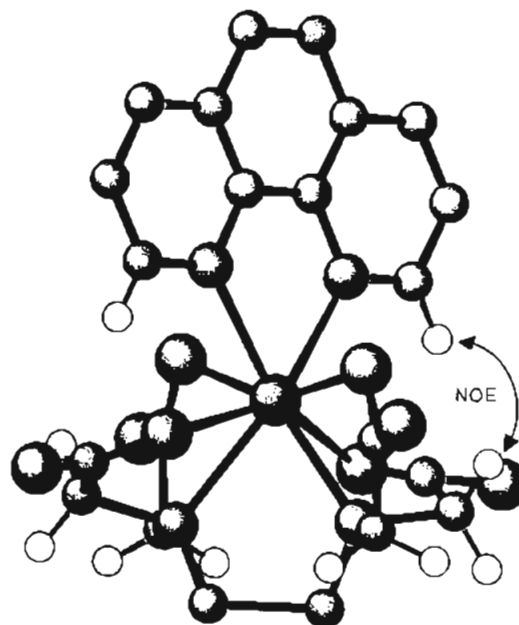
(22) The magnitudes of this parameter were confirmed by measurements at 200, 300, 400, and 500 MHz, as slightly different values, i.e., 361.68(2) and 308.36(2) Hz, were reported.<sup>11</sup>



**Figure 5.** Aromatic part of the  $^{13}\text{C}$ - $^1\text{H}$  heteronuclear correlation spectrum (11.4 T,  $\text{D}_2\text{O}$ , pD 5, room temperature, no  $^{13}\text{C}$  decoupling) for the  $[\text{Tl}(\text{cdta})(\text{D}_2\text{O})]^-/\text{phen}$  system showing correlations due to the 8-coordinate  $[\text{Tl}(\text{cdta})(\text{phen})]^-$  complex (full lines) and the dynamic 7-coordinate  $[\text{Tl}(\text{cdta})(\text{phenD})]$  complex (dotted lines).

magnitudes of the  $^3J(\text{Tl},\text{H})$  coupling constants in  $[\text{Tl}(\text{cdta})(\text{phen})]^-$  (see Table 3), the conformations of the glycine-type chelate rings have to be distinctly different from those in the complexes  $[\text{Tl}(\text{cdta})(\text{A})]$  discussed above. This is in keeping with the formulation of the phen complex having a coordination number of 8; i.e., both of the nitrogen donors of phen are coordinated. The latter is also suggested by the splitting of the resonances attributed to phen arising from coupling to the Tl spins (Figure 5 shows the appropriate section of a C-H correlation for the complex  $[\text{Tl}(\text{cdta})(\text{phen})]^-$ ). To explore further the solution structure of  $[\text{Tl}(\text{cdta})(\text{phen})]^-$ , two-dimensional nuclear Overhauser experiments were performed. The results, showing in particular a weak contact between the hydrogens ortho to the nitrogens in phenanthroline to one of the  $\text{CH}_2$  hydrogens of the pseudo-equatorial ring, suggest a somewhat distorted dodecahedron as the relevant coordination polyhedron in  $[\text{Tl}(\text{cdta})(\text{phen})]^-$ . As compared to the 7-coordinate complexes, the coordinated acetate oxygens are considerably further apart from the mean plane defined by these atoms and Tl. The changes in the conformations of the glycine-type chelates are best explained with the pseudoaxial acetates bending somewhat further forward around the central atom and the pseudo-equatorial ones bending somewhat more backward. A possible structure summarizing the findings of vicinal coupling constants and NOE distance constraints is shown in Figure 6.

**$[\text{Tl}(\text{cdta})(\text{phenH})]$ .** The second component observed in the spectra of the  $[\text{Tl}(\text{cdta})(\text{phen})]^-$  complex has  $^1\text{H}$  characteristics (see Table 3) similar to those of the system  $[\text{Tl}(\text{cdta})(\text{H}_2\text{O})]^-/[\text{Tl}(\text{cdta})(\text{OH})]^{2-}$  but significantly different  $^{13}\text{C}$  NMR parameters at a pH of ca. 5; e.g.,  $^2J(\text{Tl},\text{COO})$  couplings are 136/113 Hz in  $[\text{Tl}(\text{cdta})(\text{phenH})]$  as opposed to 167/119 Hz in  $[\text{Tl}(\text{cdta})(\text{H}_2\text{O})]^-$  at pH 6. While the former characteristics suggest a complex having a coordination number of 7, the latter indicate a coligand having medium  $\sigma$ -donor properties. As there are also additional phenanthroline resonances of appropriate intensity in the

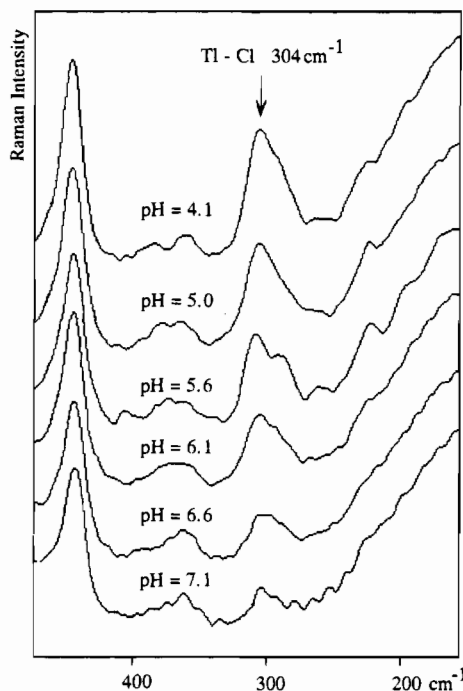


**Figure 6.** Model for the 8-coordinate complex  $[\text{Tl}(\text{cdta})(\text{phen})]^-$  (part of the cyclohexyl ring omitted) summarizing findings from NOE spectroscopy and conformation-sensitive vicinal coupling constants.

aromatic region of the  $^1\text{H}$  and  $^{13}\text{C}$  spectra (see, e.g., Figure 5), this species is formulated as  $[\text{Tl}(\text{cdta})(\text{phenH})]$ . This formulation is in agreement with the log  $K$  value of 2.77 found from the pH-monitored equilibrium measurements described above. Indeed,  $[\text{Tl}(\text{cdta})(\text{phen})]^-$  and  $[\text{Tl}(\text{cdta})(\text{phenH})]$  should be present in approximately the same concentration at pH 5, where the NMR measurements were performed. The symmetry observed for the phenH coligand in  $[\text{Tl}(\text{cdta})(\text{phenH})]$  and the absence of Tl couplings to the phen  $^1\text{H}$  and  $^{13}\text{C}$  spins indicate fast exchange on the NMR time scale of bound with free coligand and, possibly,  $\text{H}_2\text{O}$ .

In conclusion, these NMR studies provided ample evidence for the formation of stable mixed-ligand 7- and 8-coordinate Tl complexes in aqueous solution. This information is direct, where carbon- or proton-containing coligands were involved, or indirect, in the form of changes in the coupling constants between edta and cdta spins and the Tl, as in the cases of the halides.

**C. Raman Spectroscopy.** Potentiometric measurements and NMR spectra yielded indirect evidence of the coordination of halides by  $[\text{Tl}(\text{edta})]^-$ . Raman spectroscopy is one of the rare methods which allows direct observation of the ligand exchange reaction upon titration in aqueous solution. The changes in the Raman spectrum of a solution containing 0.2 M  $[\text{Tl}(\text{edta})]^-$  and 0.2 M  $\text{Cl}^-$  are shown in Figure 7 as a function of the pH values corresponding to values of the parameter  $a$  of 0.99, 1.09, 1.25, 1.50, 1.75, and 1.91. One band at  $304\text{ cm}^{-1}$  disappears from the spectrum and a new band grows in as a shoulder at  $480\text{ cm}^{-1}$  (not shown) with increasing pH values. The former band at  $304\text{ cm}^{-1}$  is assigned to the Tl-Cl vibration and the latter at  $480\text{ cm}^{-1}$  is assigned to the Tl-OH vibration on the basis of our interpretation of the titration curve. A similar pattern is observed for other simple ligands X, such as  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{N}_3^-$ , and  $\text{SCN}^-$ . The band which disappears is assigned to the Tl-X vibration. It is observed at  $207\text{ cm}^{-1}$  for  $\text{Br}^-$ ,  $176\text{ cm}^{-1}$  for  $\text{I}^-$ ,  $357\text{ cm}^{-1}$  for  $\text{N}_3^-$ , and  $253\text{ cm}^{-1}$  for  $\text{SCN}^-$ . In each case, a new band at ca.  $480\text{ cm}^{-1}$  appears in the spectrum, assigned to the Tl-OH vibration. The assignment of the Tl-X vibration is supported by the shift of the band upon halide substitution. This shift is estimated to  $93\text{ cm}^{-1}$  for  $\text{Cl}^-/\text{Br}^-$  and  $130\text{ cm}^{-1}$  for  $\text{Cl}^-/\text{I}^-$  substitution, respectively, considering localized

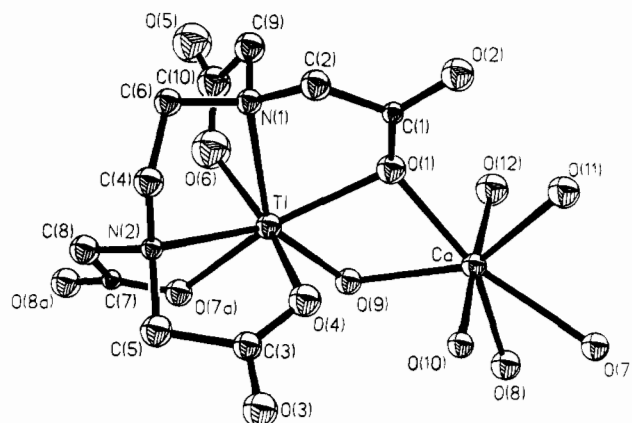


**Figure 7.** Raman spectra of a solution 0.2 M  $[\text{Tl}(\text{edta})]^-$ , 0.2 M  $\text{Cl}^-$  (0.8 M  $\text{NaNO}_3$ ) at different pHs (adjusted by addition of  $\text{NaOH}$ ).

normal coordinates and the mass change, assuming the same force constants. This estimate is in good agreement with the observed frequency differences of 97 and  $128\text{ cm}^{-1}$ .  $\text{Tl}-\text{Cl}$  vibrations of  $\text{Tl}(\text{III})$  chloro complexes in aqueous solution are reported<sup>23</sup> at  $327\text{ cm}^{-1}$  for  $\text{TlCl}_2^+$ , at  $320\text{ cm}^{-1}$  for  $\text{TlCl}_2^+$ , at  $313\text{ cm}^{-1}$  for  $\text{TlCl}_3$ , at  $309\text{ cm}^{-1}$  for  $\text{TlCl}_4^-$ , and at  $273\text{ cm}^{-1}$  for  $\text{TlCl}_6^{3-}$ , in agreement with our assignment. The frequencies of the  $\text{Tl}-\text{Br}$  and  $\text{Tl}-\text{I}$  vibrations for solid complexes are reported<sup>24</sup> at  $193-198$  and  $149-198\text{ cm}^{-1}$ , respectively. The  $\nu_a(\text{NNN})$  vibration of  $\text{N}_3^-$  at  $2070\text{ cm}^{-1}$  is observed in addition to the  $\text{Tl}-\text{N}$  vibration at  $357\text{ cm}^{-1}$  for the  $[\text{Tl}(\text{edta})(\text{N}_3)]^{2-}$  complex, in agreement with those for other azido complexes. The localization of  $\nu_s(\text{NNN})$  and  $\delta(\text{NNN})$  at ca.  $1200$  and  $600\text{ cm}^{-1}$  was not possible. In the spectra of the solutions containing  $[\text{Tl}(\text{edta})]^-$  and  $\text{SCN}^-$  four further bands are observed at  $2136$ ,  $2053$ ,  $743$ , and  $714\text{ cm}^{-1}$ . The intensity of the peaks at  $2136$  and  $714\text{ cm}^{-1}$  decreases in the spectra at  $a = 1.75$  and  $1.91$ , whereas the peaks at  $2053$  and  $742\text{ cm}^{-1}$  observed in the spectrum of all the solutions gain intensity. The two former bands are assigned respectively to  $\nu(\text{CN})$  and  $\nu(\text{C}-\text{S})$  of bound  $\text{SCN}^-$ ;<sup>25</sup> the latter two, to those of free  $\text{SCN}^-$ . The high frequency of the  $\nu(\text{CN})$  vibration ( $>2100\text{ cm}^{-1}$ ) is indicative for S-bonding of the  $\text{SCN}^-$  ligand. S-bonding of  $\text{SCN}^-$  to  $\text{Tl}^{3+}$  was also found by Blixt et al. on the basis of NMR measurements.<sup>26</sup> Free  $\text{SCN}^-$  is present in these solutions arising from partial reduction of  $\text{Tl}(\text{III})$  to  $\text{Tl}(\text{I})$  rather than from incomplete complex formation as is indicated by the value of the equilibrium constant in Table 2.

**D. Crystal Structures.** In this study the complexes  $\text{Ca}[\text{Tl}(\text{edta})(\text{OH})]\cdot 3\text{H}_2\text{O}$  and  $[\text{Tl}(\text{tpen})(\text{NO}_3)]_2[\text{ClO}_4]_2$  could structurally be characterized by X-ray diffraction methods.

**$\text{Ca}[\text{Tl}(\text{edta})(\text{OH})]\cdot 3\text{H}_2\text{O}$ .** An ORTEP view of the complex  $\text{Ca}[\text{Tl}(\text{edta})(\text{OH})]\cdot 3\text{H}_2\text{O}$  is given in Figure 8. The compound



**Figure 8.** ORTEP view of the complex  $\text{Ca}[\text{Tl}(\text{edta})(\text{OH})]\cdot 3\text{H}_2\text{O}$ .

exists in the form of infinite chains where a 7-coordinated Ca atom links two individual Tl units. The Ca coordination sphere consists of three  $\text{H}_2\text{O}$  molecules, the bridging  $\text{OH}^-$  ligand, and three (1 + 2) carboxylate oxygens of adjacent  $\text{Tl}(\text{edta})$  moieties. The coordination polyhedron of the Tl center consists of a tetrahedrally distorted trigonal prism, formed by the six donors of the edta ligand, face-capped by the hydroxy ligand. The same type of 7-coordination had been found for the related cyanide complex  $\text{Na}_2[\text{Tl}(\text{edta})(\text{CN})]\cdot 3\text{H}_2\text{O}$ .<sup>11</sup> It can be seen from the two Figures 8 in ref 11 and in this work that, in these two structurally characterized complexes, the edta ligand occupies only slightly more than half of the coordination sphere. As far as steric hindrance is concerned, it seems also possible that a further increase in the coordination number from 7 to 8 is feasible. Indeed, a low-quality structure determination (due to extensive decomposition during measurement) of  $\text{Na}[\text{Tl}(\text{edta})(\text{en})]\cdot 6\text{H}_2\text{O}$  showed that, in addition to the six donors of the edta ligand, both nitrogens of the ethylenediamine are coordinated to Tl; i.e.,  $\text{CN} = 8$ .<sup>12</sup>

**$[\text{Tl}(\text{tpen})(\text{NO}_3)]_2[\text{ClO}_4]_2$ .** Octacoordination is also present in the tpen complex salt  $[\text{Tl}(\text{tpen})(\text{NO}_3)]_2[\text{ClO}_4]_2$ , which was isolated after dissolution of  $\text{tpen}\cdot 4\text{HClO}_4$  in a solution of  $\text{Tl}(\text{NO}_3)_3$  in nitric acid. The structural study exhibits a coordination polyhedron that can be described as a distorted dodecahedron, as found, e.g., in  $\text{Mo}(\text{CN})_8^{2-}$ .<sup>27</sup> An ORTEP view of the complex cation is presented in Figure 9. Presumably, due to the low solubility of this particular combination of anions, it contains perchlorate anions, despite the large concentration of nitrate present in solution. The presence of the nitrate ligand in this complex raises, of course, a question as to the thermodynamic stability of  $\text{Tl}(\text{III})$  nitrate complexes and the appropriateness of choosing  $\text{NaNO}_3$  as an "inert" electrolyte in the determination of the stability constants given in Table 2. However, dissolving crystals of  $[\text{Tl}(\text{tpen})(\text{NO}_3)]_2[\text{ClO}_4]_2$  in  $\text{D}_2\text{O}$  leads to an  $^1\text{H}$  NMR spectrum where heteronuclear coupling to the thallium spins can be observed for all the protons in the complex. The magnitudes of this parameter do not change when free  $\text{NO}_3^-$  is added up to a concentration of ca. 3 M. This observation seems consistent with either weak or very strong nitrate coordination. The latter possibility, however, is ruled out by the substitution experiments monitored by the potentiometric measurements summarized in Table 2.

For group 13 of the periodic table, there are now structural data available for edta complexes of  $\text{Al}(\text{III})$ ,  $\text{Ga}(\text{III})$ ,  $\text{In}(\text{III})$ ,

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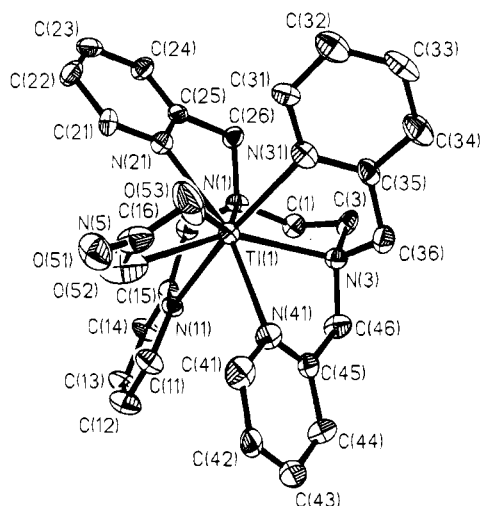
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**Table 4.** Comparison of Structural Data for M<sup>III</sup>(edta) Complexes with Metals of the Boron Group

complex salt	d <sup>n</sup>	CN		radius, <sup>a</sup> Å	⟨r(M–N)⟩, Å	⟨r(M–O)⟩, Å	⟨(O–M–N)⟩, deg	⟨(N–M–N)⟩, deg	ref
		edta	total						
K[Al(edta)]·2H <sub>2</sub> O	d <sup>0</sup>	6	6	0.68	2.05	1.88	83.2	87.5	28a
[Ga(Hedta)(H <sub>2</sub> O)]	d <sup>10</sup>	5	6	0.76	2.14	1.96	82.7	83.8	28b
[Na <sub>3</sub> [In(edta)(SO <sub>3</sub> )]·4H <sub>2</sub> O]	d <sup>10</sup>	6	7	1.00	2.35	2.21	74.7	76.6	28c
Ca[Tl(edta)(OH)]·3H <sub>2</sub> O	d <sup>10</sup>	6	7	1.08	2.39	2.40	70.2	76.9	this work
Na <sub>2</sub> [Tl(edta)(CN)]·3H <sub>2</sub> O	d <sup>10</sup>	6	7	1.08	2.41	2.36	69.9	75.8	11

<sup>a</sup> Ionic radii for the given charge and CN.

**Figure 9.** ORTEP view of the complex cation [Tl(tpen)(NO<sub>3</sub>)]<sup>2+</sup>.

and Tl(III); see Table 4. These data show that an increase in the metal ionic radius causes an increase in the metal–donor atom bond length and a decrease in the N–M–N and N–M–O angles, as expected. However, it is interesting to note that the increase in the M(III)–O bond length is more than 2 times larger than that of M(III)–N, reflecting the nature of the metal centers. As expected for the harder Al(III), a smaller bond length is found with O instead of N, whereas these are approximately the same in the complexes [Tl(edta)(A)]<sup>2–</sup>, A = OH and CN. The reduction in the angles N–M–N and N–M–O as one proceeds from Al(III) to Tl(III) reflects the inability of the edta ligand to fully encumber the larger In(III) and Tl(III) metal centers, leaving enough space for the coordination of additional ligands. Thus indium reaches a CN = 7 in Na<sub>3</sub>[In(edta)(SO<sub>3</sub>)]·4H<sub>2</sub>O, and thallium a CN = 7 in Ca[Tl(edta)(OH)]·3H<sub>2</sub>O and Na<sub>2</sub>[Tl(edta)(CN)]·3H<sub>2</sub>O, and even a CN = 8 in Na[Tl(edta)(en)]·6H<sub>2</sub>O and [Tl(tpen)(NO<sub>3</sub>)]<sub>2</sub>[ClO<sub>4</sub>]<sub>2</sub>.

## Conclusions

Tl<sup>3+</sup> forms complexes of the type [TlX<sub>n</sub>]<sup>(3–n)+</sup>, n = 1–6, with monodentate ligands X<sup>–</sup> having the following sequence of K<sub>1</sub> values: Cl<sup>–</sup> < Br<sup>–</sup> < I<sup>–</sup> < CN<sup>–</sup>, whereas N<sub>3</sub><sup>–</sup> and SCN<sup>–</sup> are quite similar to Cl<sup>–</sup>.<sup>16,26</sup> This behavior is similar to that of Hg<sup>2+</sup>, where, however, N<sub>3</sub><sup>–</sup> and SCN<sup>–</sup> are found to be closer to Br<sup>–</sup>.<sup>29</sup> In solution, the very stable complex [Tl(edta)]<sup>–</sup> shows a strong tendency to bind the same ligands, as does Tl<sup>3+</sup>, maintaining a very similar sequence in the magnitude of the

stability constants (Cl<sup>–</sup> < N<sub>3</sub><sup>–</sup> < SCN<sup>–</sup> < Br<sup>–</sup> < I<sup>–</sup> < CN<sup>–</sup>). In these mixed-ligand complexes one or two coordination sites can be occupied, but in the second case only bidentate ligands seem to be effective. Similar behavior is observed for the analogous thallic complexes of *trans*-cdta (Cl<sup>–</sup> < SCN<sup>–</sup> < Br<sup>–</sup> < N<sub>3</sub><sup>–</sup> < I<sup>–</sup>). Similar mixed-ligand complexes are found also with the Tl(III) complex of the hexadentate polyamine tpen. With all monodentate ligands, the constant K for [Tl(tpen)]<sup>3+</sup> is larger with respect to those of the other two Tl(III) complexes. This is probably mainly due to the large and positive value of its charge 3+ instead of 1– and less to steric reasons. In this case the stability sequence is SCN<sup>–</sup> < Cl<sup>–</sup> < Br<sup>–</sup> < N<sub>3</sub><sup>–</sup> < I<sup>–</sup>. On the contrary, with bidentate ligands it was only possible to obtain complexes with phen and ox<sup>2–</sup>. In this case, to reach a larger K value, it was necessary to take an anionic ligand with charge 2–, which, on complex formation, also contributed a large favorable entropic term by charge neutralization. The lower value in the case of phen can be explained by steric strain between the voluminous phen and the bound tpen which contains four bulky pyridine rings.

In summary, it can be said that invaluable insight into the coordination behavior of thallium(III), in particular with respect to higher coordination numbers, could be obtained by the employed combination of potentiometric equilibrium measurements and Raman and multinuclear and multidimensional NMR spectroscopy in solution as well as X-ray crystallography for the solids.

## Experimental Section

**Safety Note.** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts should be prepared, and these should be handled with great caution. Thallium is highly poisonous and should also be handled with caution.<sup>30</sup>

**Reagents.** Tl(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O (Fluka, purum), H<sub>4</sub>edta (Merck, rein), Na<sub>2</sub>H<sub>2</sub>edta (Komplexon III, Siegfried), H<sub>4</sub>cdta (Geigy), and ethylenediamine (Fluka, puriss. p.a) were used for synthesis without further purification. The synthesis of tpen·4HClO<sub>4</sub> was described previously.<sup>13b</sup> For the equilibrium measurements, water was bidistilled under nitrogen and the ligands added were purified and controlled by alkalimetric titrations. In all syntheses, the base was added slowly under stirring in order to avoid a strong local alkalization and the precipitation of brown Tl(OH)<sub>3</sub>.

**H[Tl(edta)]·H<sub>2</sub>O.** Tl(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O was dissolved in a small amount of 1 M nitric acid, and an equivalent amount of H<sub>4</sub>edta was added with stirring. Slow dilution with water completed the reaction (quantitatively due to the very high formation constant (log K<sub>1</sub> = 37.8; with K<sub>1</sub> = [ML]/([M][L])<sup>31</sup>) of the complex). Double recrystallization from 0.1 M solution of nitric acid yielded white, very fine needles or powders of high purity. Aqueous solutions of this complex are subject

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to photochemical decomposition.<sup>32</sup> Mp: >164 °C dec. Anal. Calcd for C<sub>10</sub>H<sub>13</sub>N<sub>2</sub>O<sub>8</sub>Tl·H<sub>2</sub>O: C, 23.48; H, 2.96; N, 5.48; Tl, 39.95. Found: C, 23.28; H, 3.12; N, 5.49; Tl, 39.40.

**H[Tl(edta)]·3H<sub>2</sub>O.** The same procedure as for H[Tl(edta)]·H<sub>2</sub>O was used with H<sub>4</sub>edta as ligand. Double recrystallization from water yielded white or colorless scales which deposited as a hard but breakable layer on the bottom of the crystallization vessel. Also in this case photochemical decomposition occurs in aqueous solution, but 0.2 M solutions can be prepared and are stable. Mp: 158 °C dec. Anal. Calcd for C<sub>14</sub>H<sub>19</sub>N<sub>2</sub>O<sub>8</sub>Tl·3H<sub>2</sub>O: C, 27.95; H, 4.19; N, 4.66. Found: C, 27.74; H, 3.70; N, 4.69.

**Ca[Tl(edta)(OH)]·3H<sub>2</sub>O.** The high solubility of most M<sup>I</sup>[Tl(edta)] or M<sup>II</sup>[Tl(edta)(OH)] complex salts caused problems in attempts to obtain crystals suitable for X-ray analysis. An aqueous suspension of H[Tl(edta)]·H<sub>2</sub>O was used and neutralized by very slow addition, under vigorous stirring, of the correct amount of solid hydroxide or carbonate of the chosen metal M(I) or M(II). Crystallization was obtained by slow evaporation of the solution at room temperature. All attempts to obtain M<sup>I</sup>[Tl(edta)] (with M(I) = Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, Ag<sup>+</sup>, and Me<sub>4</sub>N<sup>+</sup>) or M<sup>II</sup>[Tl(edta)(OH)] (with M(II) = Sr<sup>2+</sup> and Ba<sup>2+</sup>) resulted in the formation of powdery or glassy products. Only with the use of the Tl<sup>+</sup> and Ca<sup>2+</sup> cations were Tl<sup>I</sup>[Tl(III)(edta)] and Ca[Tl(edta)(OH)]·3H<sub>2</sub>O obtained as colorless crystals. The former decomposed within 1 h of the X-ray measurements.

**Na[Tl(edta)(en)]·6H<sub>2</sub>O.** This complex was obtained by starting from an approximately 1 M Tl(NO<sub>3</sub>)<sub>3</sub> solution, containing the same molar concentration of nitric acid in order to avoid Tl<sup>3+</sup> hydrolysis. Its metal content was determined with edta using xylenol orange as indicator. To a portion of the above solution (12.1 mmol or 10 mL of 1.21 M Tl(NO<sub>3</sub>)<sub>3</sub>) were added the exact equimolar amount of solid (12.1 mmol, 4.5 g) Na<sub>2</sub>H<sub>2</sub>edta and 3 times the equimolar amount of a NaOH solution (36.3 mL, 1 M). The obtained solution (pH ≈ 6) was mixed with the stoichiometric amount of ethylenediamine (0.73 g, 12.1 mmol) under strong N<sub>2</sub> bubbling. Crystallization occurred after slow evaporation of the solution. Anal. Calcd for C<sub>12</sub>H<sub>20</sub>N<sub>4</sub>O<sub>8</sub>NaTl: C, 25.04; H, 3.50; N, 9.73; Tl, 35.51. Found: C, 24.28; H, 3.54; N, 9.25; Tl, 35.08.

**[Tl(tpen)(NO<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub>.** Equimolar amounts of Tl(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O and tpen·4HClO<sub>4</sub> were suspended in a small amount of 1 M nitric acid. The stirred suspension was diluted very slowly with water until all of the solid had dissolved. Large colorless prisms appeared in the filtered solution upon standing at room temperature. Aqueous solutions of this complex are photochemically stable. Mp: 153 °C dec. Anal. Calcd for C<sub>26</sub>H<sub>28</sub>Cl<sub>2</sub>N<sub>7</sub>O<sub>11</sub>Tl: C, 35.10; H, 3.17; N, 11.02; Tl, 22.97. Found: C, 35.03; H, 3.21; N, 11.10; Tl, 23.41.

**Equilibrium Measurements.** Potentiometric pH measurements were performed in a thermostated air-tight jacket glass titration vessel (5 mL), fitted with a glass and a calomel reference electrode (0.9 M NaClO<sub>4</sub>, 0.1 M NaCl or 0.9 M NaNO<sub>3</sub>, 0.1 M NaCl, I = 1.00 M). Titrations were performed under an atmosphere of N<sub>2</sub>, which was purified and equilibrated with water vapor by passage through a 1.00 M NaClO<sub>4</sub> or NaNO<sub>3</sub> solution. The system was kept at a constant temperature of 25.00 ± 0.01 °C by circulating thermostated water through the outer jacket of the vessel. All solutions were adjusted to an ionic strength of I = 1.00 M by addition of NaClO<sub>4</sub> or NaNO<sub>3</sub>. Measurements were carried out using Mettler DV11 and Metrohm Dosimat 665 burets and an Orion Research SA720 pH meter calibrated with standard strong acid at the same ionic strength. Typically five titrations were performed, recording between 60 and 180 points for each measurement. The negative logarithm of the ionic product of water, pK<sub>w</sub>, was calculated from the pH values of the strong base solution obtaining 13.67 ± 0.02 and 13.65 ± 0.02 at 25 °C for I = 1.00 (NaClO<sub>4</sub> and NaNO<sub>3</sub>, respectively). The determination of the stability constants of mixed-ligand complexes MLA from ML and A required a knowledge of the protonation constants of A, K<sub>i</sub> = [H<sub>i</sub>A]/([H<sub>i-1</sub>A][H<sup>+</sup>]) (except for the halides and SCN<sup>-</sup>), and [ML(OH)]. These values were obtained by separate potentiometric titration of the ligand A and [Tl(L)(H<sub>2</sub>O)] at different concentrations (4–6 mM) in the

**Table 5.** Experimental Data for the X-ray Diffraction Studies

	Ca[Tl(edta)(OH)]·3H <sub>2</sub> O	[Tl(tpen)(NO <sub>3</sub> )](ClO <sub>4</sub> ) <sub>2</sub>
empirical formula	C <sub>10</sub> H <sub>13</sub> CaN <sub>2</sub> O <sub>9</sub> Tl·3H <sub>2</sub> O	C <sub>26</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>7</sub> O <sub>11</sub> Tl
mol wt	603.72	889.82
cryst syst	monoclinic	monoclinic
space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /c
a, Å	13.744(8)	12.718(6)
b, Å	9.141(2)	13.640(7)
c, Å	13.752(0)	18.883(9)
β, deg	100.71(0)	108.84(4)
V, Å <sup>3</sup>	1697.8	3100(3)
Z	4	4
Q <sub>calc</sub> , g cm <sup>-3</sup>	2.320(4)	1.906
F <sub>000</sub>	1160	1744
R <sup>a</sup>	0.075	0.036
R <sub>w</sub> <sup>b</sup>	0.086	0.051
no. of measd reflns	3015	3273
no. of obsd reflns	2082 with I > 3σ(I)	2243 with F > 4σ(F)

<sup>a</sup> R = Σ||F<sub>o</sub> - |F<sub>c</sub>||/Σ|F<sub>o</sub>|. <sup>b</sup> R<sub>w</sub> = Σw<sup>1/2</sup>(|F<sub>o</sub> - |F<sub>c</sub>||)/Σw<sup>1/2</sup>|F<sub>o</sub>|, w = 2/σ<sup>2</sup>(F<sub>o</sub>).

**Table 6.** Fractional Atomic Coordinates (Å) and Equivalent Thermal Parameters (Å<sup>2</sup>) for Ca[Tl(edta)(OH)]·3H<sub>2</sub>O

	x	y	z	U <sub>eq</sub> <sup>a</sup>
Tl	0.23336(7)	-0.00987(9)	0.26784(6)	0.0234(3)*
Ca	0.2398(4)	0.7343(5)	0.4805(3)	0.023(2)*
N(1)	0.342(1)	0.191(2)	0.318(1)	0.021(4)
N(2)	0.145(1)	0.194(2)	0.185(1)	0.016(4)
O(1)	0.313(1)	0.962(2)	0.438(1)	0.028(4)
O(2)	0.389(1)	0.415(2)	0.071(2)	0.032(4)
O(3)	0.052(1)	0.643(2)	0.175(1)	0.032(4)
O(4)	0.103(1)	0.068(2)	0.353(1)	0.031(4)
O(5)	0.492(2)	0.556(3)	0.338(2)	0.059(6)
O(6)	0.360(2)	0.988(3)	0.172(2)	0.058(5)
O(7)	0.163(1)	0.925(2)	0.100(1)	0.027(4)
O(8)	0.160(1)	0.488(2)	0.451(1)	0.033(4)
O(9)	0.215(1)	0.768(2)	0.305(1)	0.025(4)
O(10)	0.095(1)	0.860(2)	0.493(1)	0.021(3)
O(11)	0.302(1)	0.657(2)	0.137(1)	0.031(4)
O(12)	0.391(1)	0.623(2)	0.483(1)	0.040(5)
C(1)	0.350(1)	0.076(2)	0.480(1)	0.014(4)
C(2)	0.342(2)	0.216(3)	0.423(2)	0.026(5)
C(3)	0.030(2)	0.125(2)	0.299(2)	0.021(5)
C(4)	0.191(2)	0.321(3)	0.238(2)	0.024(5)
C(5)	0.038(2)	0.178(3)	0.192(2)	0.030(6)
C(6)	0.301(2)	0.319(3)	0.256(2)	0.022(5)
C(7)	0.156(1)	0.031(2)	0.040(1)	0.014(4)
C(8)	0.151(2)	0.187(3)	0.077(2)	0.028(5)
C(9)	0.442(2)	0.149(3)	0.298(2)	0.030(6)
C(10)	0.434(2)	0.062(3)	0.205(2)	0.038(6)

<sup>a</sup> U<sub>eq</sub> = 1/3Σ<sub>i</sub>U<sub>ij</sub>a<sub>i</sub>a<sub>j</sub>(a<sub>i</sub>a<sub>j</sub>); the asterisks denote isotropic temperature factors.

corresponding medium, using the programs KONST<sup>33</sup> and SUPERQUAD.<sup>34</sup> The values obtained are summarized in Table 1, together with a list of abbreviations for the ligands. The constants for the mixed-ligand complexes K = [Tl(L)(A)]/([Tl(L)][A]) were obtained from titrations of [Tl(L)(H<sub>2</sub>O)] in the presence of the ligand A. The calculations were performed with the program SUPERQUAD, taking into consideration the presence of the hydroxo complex [Tl(L)(OH)]. The computed constants were then checked with the program HAL-TAFALL,<sup>35</sup> which allowed the simulation of the experimental curve. The use of two different inert salts arose from the fact that [Tl(tpen)(H<sub>2</sub>O)]<sup>3+</sup> and H(phen)<sup>+</sup> precipitated in the presence of ClO<sub>4</sub><sup>-</sup>.

**NMR Measurements.** <sup>1</sup>H NMR spectra were recorded on Bruker AMX 500 and AMX 400 spectrometers operating at 500.13 and 400.13 MHz, respectively, while <sup>13</sup>C NMR spectra were obtained at 125.6 and

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**Table 7.** Fractional Atomic Coordinates (Å) and Equivalent Isotropic Thermal Parameters (Å<sup>2</sup>) for [Ti(tpen)(NO<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub>

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Ti	0.3223(1)	0.2179(1)	0.1741(1)	0.033(1)
N(1)	0.3787(7)	0.1570(7)	0.0700(4)	0.036(3)
C(1)	0.2797(9)	0.1206(8)	0.0097(6)	0.042(5)
C(3)	0.1961(8)	0.0701(9)	0.0392(6)	0.045(5)
N(3)	0.1603(7)	0.1370(6)	0.0899(5)	0.041(4)
N(11)	0.3364(7)	0.3545(6)	0.0972(5)	0.036(4)
C(11)	0.2996(10)	0.4437(9)	0.1036(6)	0.048(5)
C(12)	0.2985(11)	0.5187(9)	0.0548(7)	0.061(6)
C(13)	0.3416(11)	0.5001(9)	-0.0023(7)	0.058(6)
C(14)	0.3788(10)	0.4088(9)	-0.0108(7)	0.052(5)
C(15)	0.3780(9)	0.3381(9)	0.0419(7)	0.045(5)
C(16)	0.4317(9)	0.2372(8)	0.0416(6)	0.038(4)
N(21)	0.5150(7)	0.1757(7)	0.2168(5)	0.036(4)
C(21)	0.5938(10)	0.2094(8)	0.2785(6)	0.039(5)
C(22)	0.7024(9)	0.1865(10)	0.2954(7)	0.050(5)
C(23)	0.7376(10)	0.1285(8)	0.2487(7)	0.049(5)
C(24)	0.6582(10)	0.0931(9)	0.1850(6)	0.045(5)
C(25)	0.5488(9)	0.1150(8)	0.1713(6)	0.039(5)
C(26)	0.4600(8)	0.0793(8)	0.1023(6)	0.041(4)
N(31)	0.2940(9)	0.0651(7)	0.2254(5)	0.043(4)
C(31)	0.3725(11)	0.0224(9)	0.2826(7)	0.052(5)
C(32)	0.3532(13)	-0.0637(10)	0.3128(8)	0.066(7)
C(33)	0.2473(14)	-0.1053(9)	0.2849(8)	0.066(7)
C(34)	0.1693(13)	-0.0609(10)	0.2263(8)	0.064(6)
C(35)	0.1943(10)	0.0242(9)	0.1981(7)	0.045(5)
C(36)	0.1091(9)	0.0792(9)	0.1364(6)	0.047(5)
N(41)	0.1502(8)	0.3018(7)	0.1671(6)	0.046(4)
C(41)	0.1390(11)	0.3718(10)	0.2152(8)	0.060(6)
C(42)	0.0529(11)	0.4373(9)	0.1959(9)	0.059(7)
C(43)	-0.0252(13)	0.4329(11)	0.1266(11)	0.081(8)
C(44)	-0.0149(10)	0.3566(10)	0.0778(8)	0.067(6)
C(45)	0.0742(10)	0.2933(8)	0.1017(7)	0.045(5)
C(46)	0.0850(10)	0.2129(8)	0.0497(6)	0.049(5)
N(5)	0.3941(9)	0.3250(10)	0.3210(7)	0.065(6)
O(51)	0.4125(8)	0.3755(7)	0.3765(5)	0.074(4)
O(52)	0.4020(9)	0.3637(9)	0.2617(5)	0.096(5)
O(53)	0.3662(10)	0.2375(9)	0.3156(9)	0.111(7)
Cl(1)	0.0548(3)	0.2107(2)	0.3482(2)	0.065(2)
O(11)	0.1546(6)	0.1595(7)	0.3796(7)	0.236(14)
O(12)	0.0118(10)	0.1906(10)	0.2713(3)	0.153(8)
O(13)	-0.0245(8)	0.1772(9)	0.3799(6)	0.121(6)
O(14)	0.0737(9)	0.3116(4)	0.3612(5)	0.105(6)
Cl(2)	0.2654(3)	0.6824(2)	0.4808(2)	0.065(2)
O(21)	0.1710(6)	0.6412(7)	0.4276(5)	0.146(8)
C(22)	0.2381(11)	0.7092(11)	0.5445(5)	0.170(11)
O(23)	0.2966(9)	0.7672(6)	0.4503(7)	0.129(8)
O(24)	0.3529(6)	0.6143(6)	0.4970(6)	0.089(5)

50.2 MHz on the AMX 500 and Bruker AC 200 instruments. Chemical shifts ( $\delta$ , ppm) are given relative to internal DSS for <sup>1</sup>H and <sup>13</sup>C; coupling constants are in Hz.

Heteronuclear correlation experiments (<sup>13</sup>C/<sup>1</sup>H) were recorded with proton observation using the seven-pulse HMQC sequence<sup>36</sup> suitable for phase-sensitive representation, where no <sup>13</sup>C decoupling was employed during acquisition. Heteronuclear long-range correlations on the full frequency range of carbon resonances were measured by employing the HMBC sequence,<sup>37</sup> whereas selective correlations between only the carboxylate carbons and protons were obtained with

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the four-pulse HMQC sequence in which the first <sup>13</sup>C pulse had been replaced by a 2 ms half-Gaussian-shaped pulse. Phase-sensitive homonuclear correlation experiments (NOESY<sup>38</sup> with a mixing time of 500 ms and double-quantum filtered COSY<sup>39</sup>) were performed using the TPPI method.<sup>40</sup>

**Raman Spectra.** These were measured on a Bruker IFS-66 FT-IR spectrophotometer equipped with a Raman unit. A 300 mW Nd-YAG laser was used as the energy source. The line positions are estimated to be accurate to  $\pm 4$  cm<sup>-1</sup> at 10 scans for solid and  $\pm 8$  cm<sup>-1</sup> at 500–1000 scans for dissolved samples. The measurements in water were performed on 0.2 M solutions in order to minimize the measuring time.

**X-ray Measurements: Determination of the Structures of (a) Ca-[Ti(edta)(OH)]·3H<sub>2</sub>O and (b) [Ti(tpen)(NO<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub>.** The lattice parameters and space groups were determined in a first step with precession measurements. These quantities were checked and all data collected with a second crystal on a SYNTEX P2<sub>1</sub> four-circle diffractometer for (a) and a Picker FACS-I automated diffractometer upgraded by Stoe<sup>41</sup> for (b), using monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The cell constants were calculated from the least-squares refinement of 25 well-centered reflections: (a)  $25^\circ \leq 2\theta \leq 30^\circ$  (strong reflections at  $2\theta = 6.4^\circ$  were also taken into account); (b)  $16^\circ \leq 2\theta \leq 23^\circ$ . The stability of the crystal was checked by recording periodically three suitable orthogonal standard reflections. During the measurement (at 20 °C) we observed for (a) in the interval  $1^\circ \leq 2\theta \leq 50^\circ$  a weak decay and for (b) in the interval  $1^\circ \leq 2\theta \leq 45^\circ$  no decay. The determination of the structures was accomplished by standard Patterson and Fourier methods (heavy atom method) with the XTAL 3.2-program package<sup>42</sup> on a CDC Cyber 855 for (a) and with the SHELXTL-Plus system<sup>43</sup> on a MicroVAX II for (b). Only thallium, calcium, and sodium atoms could be refined anisotropically for (a). In structure (b) the two perchlorate ions were refined as tetrahedral groups. The hydrogen atoms could be located in a subsequent difference density map after isotropic refinement of the structure. The final refinement was accomplished with anisotropic displacement parameters for all non-H atoms and calculated isotropic displacement parameters for H atoms.

The crystal data are given in Table 5; fractional atomic coordinates and equivalent isotropic temperature factors are given in Tables 6 and 7. The numbering schemes are shown in Figures 8 and 9. Fractional coordinates for hydrogen atoms of (b) and anisotropic thermal parameters for the two structures are given in the supplementary material.

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**Supplementary Material Available:** Tables S1–S4, giving <sup>13</sup>C and <sup>1</sup>H NMR data and Tables S5–S11, giving complete bond lengths and angles, anisotropic thermal parameters, and fractional coordinates for the hydrogen atoms of [Ti(tpen)(NO<sub>3</sub>)](ClO<sub>4</sub>)<sub>2</sub> (10 pages). Ordering information is given on any current masthead page.

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