The Stability of Metal N,N,N',N'-Tetrakis(2-aminoethyl)ethane-1,2-diamine (= penten) Complexes and the X-Ray Crystal Structure of [Tl(NO₃)(penten)](NO₃)₂

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Complex formation between N,N,N',N'-tetrakis(2-aminoethyl)ethane-1,2-diamine (penten) and the metal ions Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ag^+, Pb^{2+}, and Tl^{3+} (in 1.00M NaNO₃ and 25°) was investigated by potentiometry and spectrophotometry. These are the first reported values of the stability constants for this ligand with Ag^+, Pb^{2+}, and Tl^{3+}. The X-ray crystal structure of [Tl(NO₃)(penten)](NO₃)₂ was determined. In this structure, Tl^{3+} shows a coordination number of seven made up of the six N-donors and one O-atom of NO_3^-.

1. Introduction. – Thallium(III) hydrolyzes above pH 1 and, for this reason, few equilibrium constants have been determined [1]. As Tl^{3+} forms heptacoordinate complexes, we investigated the equilibria between Tl^{3+} and the hexadentate ligand N,N,N',N'-tetrakis(2-aminoethyl)-1,2-diaminoethane (penten). This ligand was first synthesized by *Gauss et al.* [2]. It forms stable complexes with 3d divalent metal ions, and the corresponding stability constants (in 0.1M KCl and 20° [3]) and thermodynamic data [4][5] are known. This ligand has also been used in ligand-exchange studies [6][7]. Furthermore, the kinetics of chelate ring opening within the hexadentate Co^{3+}-penten complex with formation of [Co(penten)OH]²⁺ have been reported [8]. Additionally, poly(ethylenimines) with possible penten monomer units were studied as chelating ligands for different metal ions [9][10].

$$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2 \qquad\qquad \text{CH}_2-\text{CH}_2-\text{NH}_2$$
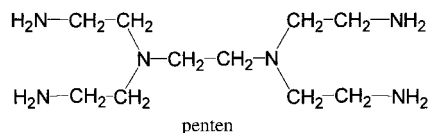
penten

This publication describes an investigation of the interactions between penten and several cations at 25° by means of pH titrations. For Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Ag^+, 1M NaNO₃ was used as the inert salt. However, for Tl^{3+} and Hg^{2+}, 1M NaClO₄ was preferred, because this medium was used for the determination of other stability constants of these metals. In the case of Cu^{2+}, also spectrophotometric measurements at $I = 1.00$M (NaClO₄) were carried out.

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To verify the general tendency of Tl^{3+} to form complexes with coordination number seven, we isolated a Tl^{3+}-penten complex salt and determined its structure by X-ray diffraction. We had previously found seven-coordinate Tl^{3+} with the ligands edta, cdta, and the polyamine *N,N,N′,N′*-tetrakis(2-pyridylmethyl)ethane-1,2-diamine (tpen). Indeed, as shown by more extensive investigations of metal-edta complexes, one should expect a coordination number of seven for trivalent cations with an ionic radius of 1.08 Å [1].

Results. – Examples of titration curves of the protonated ligand $H_4(penten)^{4+}$ in the presence of Ag^+ and Pb^{2+} are depicted in *Fig. 1*, and the calculated values for the stability constants are collected in *Table 1*. These values were obtained from the experimental data and take into account the protonation constants of penten in either $NaNO_3$ or $NaClO_4$ medium. In the case of Cu^{2+}, with $\log \beta_{ML} > 22$, the metal/ligand solutions, without excess strong acid, are acidic, with a pH value close to 2.8. This
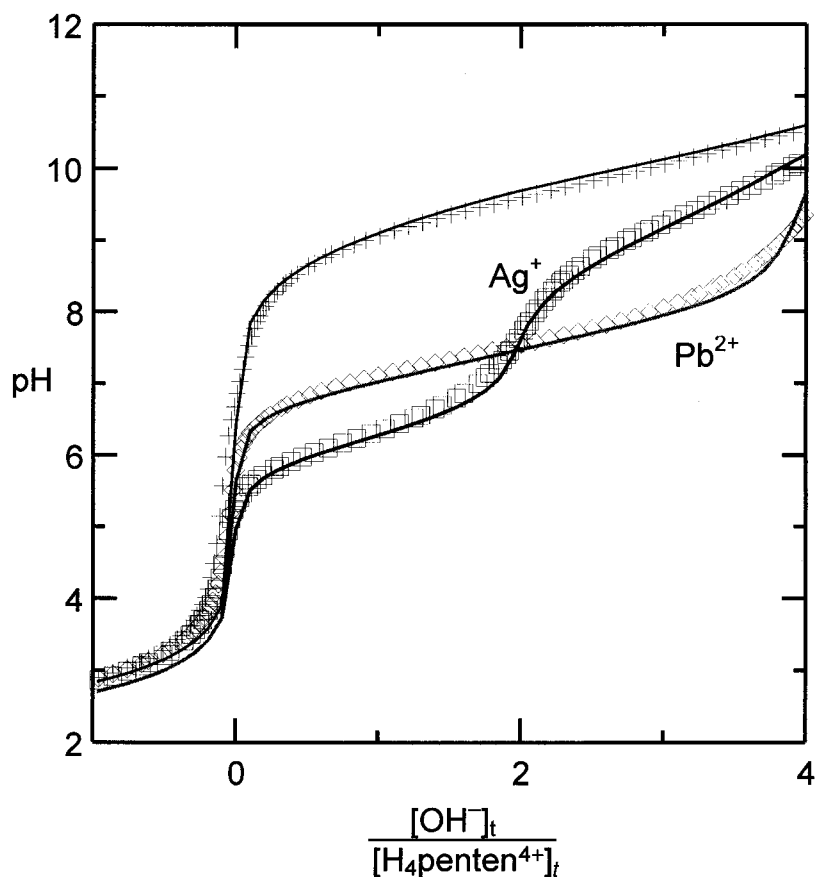

Fig. 1. *Titration curves of protonated penten $H_4penten^{4+}$ alone* (+: 2.00 mM ligand, 12.0 mM H^+, $I = 1.00$M (NaNO$_3$)) *and in presence of Ag$^+$* (□:1.97 mM) *or Pb^{2+}* (◇: 2.01 mM)

Table 1. *Overall Stability Constants* $\beta_{MH_iL} = [MH_iL]\,[M]^{-1}[L]^{-1}[H]^{-i}$ *of* MH_iL *species* ($i = 0, 1,$ and 2) *for* $L =$ *penten* (25° *and* $I = 1.00\text{M}$ (NaNO$_3$)). *Values of the protonation constants for penten* $\beta_i = [H_iL]\,[L]^{-1}\,[H]^{-i}$ *for* 1.0M (NaNO$_3$): $\log \beta_1 = 10.31(1)$, $\log \beta_2 = 20.17(1)$, $\log \beta_3 = 29.71(1)$, $\log \beta_4 = 38.49(1)$; *for* 1.0M (NaClO$_4$): $\log \beta_1 = 10.20(2)$, $\log \beta_2 = 20.25(2)$, $\log \beta_3 = 29.75(2)$, $\log \beta_4 = 38.57(2)$.

Metal ion, M^{n+}	Species, $\log \beta$ (σ)		
	[ML]	[MHL]	[MH$_2$L]
Mn^{2+}	9.33(2)	17.05(6)	
Co^{2+}	15.79(4)	23.22(3)	29.07(9)
Cu^{2+a})	23.98(7)	32.08(3)	35.55(3)
Zn^{2+}	16.66(2)	24.95(1)	
Cd^{2+}	16.64(1)	23.69(2)	
Hg^{2+a})	29.3(1)	37.76(7)	
Ag^{+b})	10.83(7)	20.37(7)	28.93(3)
Pb^{2+}	11.64(4)	19.56(4)	27.25(4)
Tl^{3+a})	37.1(3)	39.7(5)	

^{a}) For $I = 1.00\text{M}$ (NaClO$_4$) (Hg, $\log \beta$ ([HgClH$_2$(penten)]) = 43.7(2), $\log \beta$ ([Hg(OH)(penten)]) = 18.5(1)). ^{b}) $\log \beta$ (Ag$_2$L) ≤ 18.0.

indicates that [CuH$_2$L]$^{4+}$ and [CuHL]$^{3+}$ are almost completely formed, and that only negligible amounts of Cu^{2+} are present. Therefore, to obtain reliable values for the constant of CuL, spectrophotometric measurements were used. These gave us also the values of the molar absorptivity maxima of the appropriate Cu^{2+} species: [Cu(penten)]$^{2+}$: $\varepsilon_{mol} = 233.7\text{M}^{-1}\,\text{cm}^{-1}$ at $\lambda = 730$ nm; [CuH(penten)]$^{3+}$: $\varepsilon_{mol} = 202.9\text{M}^{-1}\,\text{cm}^{-1}$ at $\lambda = 725$ nm; and the unknown CuH$_2$(penten)$^{4+}$: $e_{mol} = 210.4$ M^{-1} cm^{-1} at $\lambda = 595$ nm (*Fig. 2*).

For Hg^{2+}, a solution with equimolar amounts of HgCl$_2$ and protonated ligand H$_4$penten^{4+} was titrated with strong base in presence of 0.10M NaCl adjusted to $I = 1.00$ with NaClO$_4$. Under these conditions, the main reaction is that shown in *Eqn. 1*, *i.e.*, the substitution of the Cl$^-$ anions

$$\text{HgCl}_4^{2-} + \text{H}_4\text{penten}^{4+} \rightleftharpoons \text{HgHpenten}^{3+} + 3\,\text{H}^+ + 4\,\text{Cl}^- \qquad (1)$$

in HgCl$_4^{2-}$ by the N-atoms of penten. From the overall stability constant for HgCl$_4^{2-}$ ($\log \beta_4 = 16.20$) [11], one obtains the overall constant for [Hg(Hpenten)]$^{3+}$, β([HgHpenten]$^{3+}$) = β(HgCl$_4^{2-}$) $\times \beta$(H$_4$penten^{4+}) $\times K$ (1). Upon base addition, this exchange occurs with partial formation of [HgClH$_2$penten]$^{3+}$, [Hg(penten)]$^{2+}$, and [Hg(OH)(penten)]$^+$, as shown by successive iterations and in agreement with results obtained by *Schwarzenbach* and *Moser* [3]; because we extended the measurements to higher pH values, we observed [Hg(OH)(penten)]$^+$, which had not be seen before. As discussed by *Irving* and *Stacey*, the correct interpretation of the experimental data is not simple, due to the formation of ternary metal-ligand-halogenide complexes that may also be protonated [12].

Alkalimetric titrations of the Tl^{3+}-penten complex, dissolved in strong acid solutions, show that a monoprotonated complex [Tl(Hpenten)]$^{4+}$ with p$K = 2.59$ is present. In addition, mixed complexes [TlX(Hpenten)]$^{3+}$ with X = Br ($K_1 = 10^{4.25}$) or Cl ($K_1 = 10^{2.91}$) are observed. Furthermore, the complex cation [Tl(H$_2$O)(penten)]$^{3+}$ is a very weak mono-protonic acid with p$K = 10.90$. An estimate of the stability constant
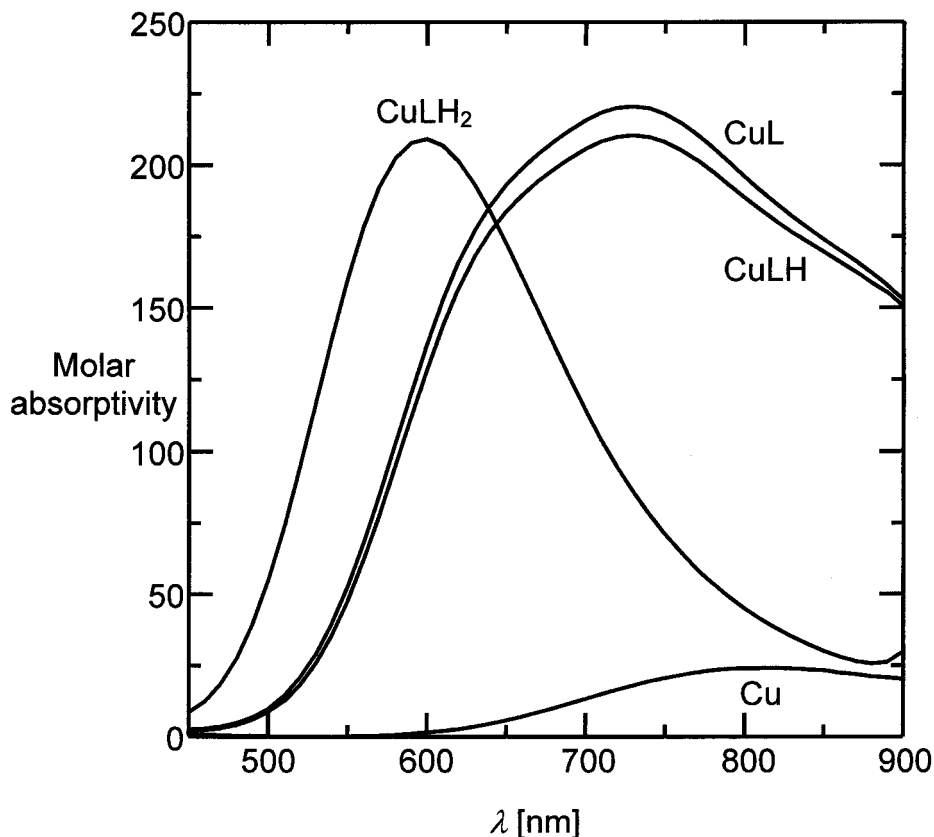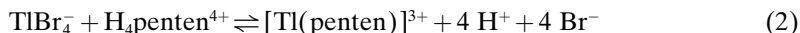
Fig. 2. *Molar absorptivity of Cu²⁺-penten species* vs. *λ*

of the penten complex was obtained from calculations with the pH data for the exchange shown in *Eqn. 2*, *i.e.*, for Tl^{3+} solutions (1.06 mM) in the presence of NaBr (0.005, 0.100, or 0.5M) at $I = 1.00$ (NaBr + NaClO$_4$).

$$TlBr_4^- + H_4penten^{4+} \rightleftharpoons [Tl(penten)]^{3+} + 4\,H^+ + 4\,Br^- \tag{2}$$

At a minimum, the species [TlBr(Hpenten)]$^{3+}$, [Tl(Hpenten)]$^{4+}$, and [Tl(penten)]$^{3+}$ are present, whereas [Tl(OH)(penten)]$^{2+}$ is important only at pH > 9. As the stability constants of the Tl(III)-Br$^-$ complexes TlBr$_n^{(3-n)+}$ are not known for $I = 1.00$, the values at $I = 4$ [13] were recalculated by the SIT (specific-ion-interaction theory) method [14] (log $\beta_1 = 8.8$, log $\beta_2 = 16.1$, log $\beta_3 = 20.9$, log $\beta_4 = 24.4$). The best value obtained for log β ([Tl(penten)]$^{3+}$) is 37.1 ± 0.3.

   Satisfactory results on the crystal structure were obtained only after collecting data from three crystals. The results could be interpreted only after the realization that the structure was disordered. The disorder arises from the two structures that are partially occupied and connected by the noncrystallographic mirror plane $(x, y, \frac{1}{2} - z)$. An *ORTEP* view of [Tl(NO$_3$)(penten)]$^{2+}$ is shown in *Fig. 3*. For clarity, only O(4) of the

coordinated NO_3^- group N(5)O(4)O(5)O(6) is shown. The two structures present are shown in the figure as black and white, with 60 and 40% occupation, respectively, to take the disorder into account. The crystallographic twofold rotation axis goes through the middle of the C(1)−C(1a) bond and Tl(1). In the solid state, the coordination polyhedron of the Tl-center consists of a distorted trigonal prism formed by the six N-atoms of penten, and one of the prism faces is capped with one O-donor of the coordinated NO_3^-. The second disordered NO_3^- is shown (in black and white) in the left part of *Fig. 3* above. The Tl−N bond distances in $[Tl(NO_3)(penten)](NO_3)_2$ are listed in *Table 2*.

Discussion. – The β values obtained (*Table 1*) for Mn^{2+}, Co^{2+}, Cu^{2+}, and Zn^{2+} follow the *Irving-Williams* order [15]. We notice small discrepancies ranging mainly from ± 0.02 to 0.25 between our data and the earlier data of *Scharzenbach* and *Moser* [3] obtained at 20° and $I = 0.1$ (KCl). These variations can be accounted for by the differences in ionic strength and inert salt (which could form complex species in the case of Cl^-) or the use of the metal sulfate (Mn^{2+}, Co^{2+}, and Cd^{2+}) in [3]. With the above metal ions as well as with H^+, SO_4^{2-} forms 1:1 complexes with a log K_1 of *ca.* 2 [16]. It is difficult to explain the great discrepancy between our value of 23.98 (*Table 1*)
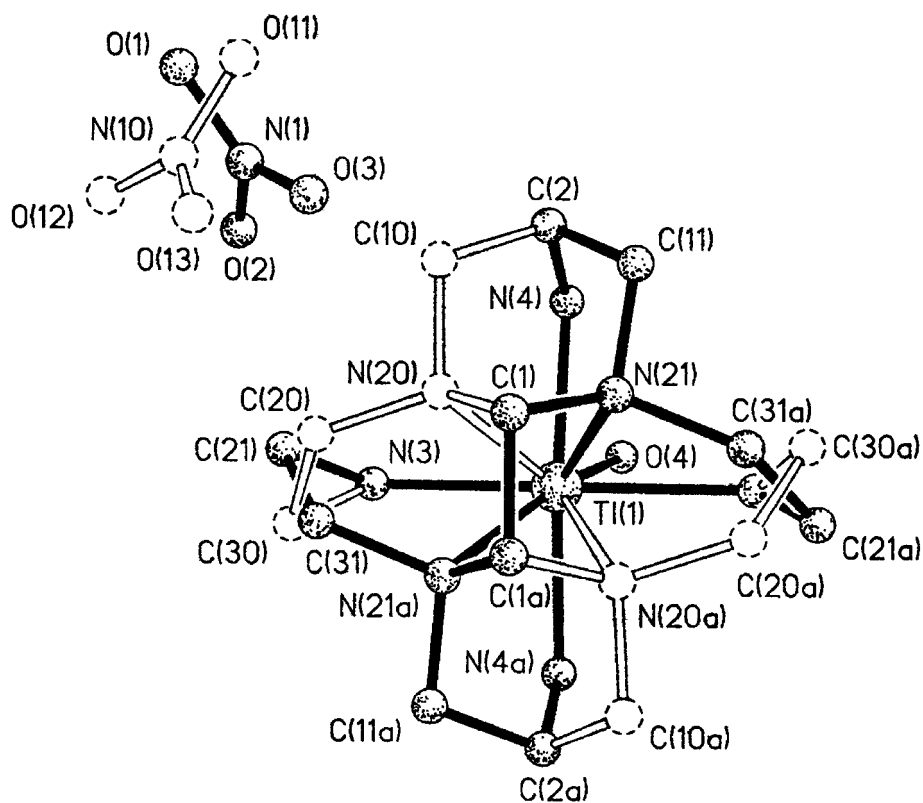

Fig. 3. *ORTEP Representation for [Tl(NO₃)(penten)](NO₃)₂*

Table 2. *Atomic Distances M−N (Å) in the Th^{III} Coordination Sphere of [Tl(NO$_3$)(penten)](NO$_3$)$_2$ and of [Tl(NO$_3$)(tpen)](NO$_3$)$_2$*

Distance	penten	tpen
Tl(1)−N(3)	2.337(22)	2.374(10)
Tl(1)−N(3a)	2.337(22)	2.389(8)
Tl(1)−N(4)	2.301(11)	2.404(9)
Tl(1)−N(4a)	2.301(11)	2.436(11)
Tl(1)−N(21)	2.437(20)	2.424(8)
Tl(1)−N(21a)	2.437(20)	2.445(9)
Tl(1)−O(4)(NO$_3$)	2.569(9)	

and the earlier value of 22.44 reported for Cu^{2+} [3] since these authors do not identify the counterion used [3]. Nevertheless our value agrees quite well with 24.25 determined for the same cation with the linear tetraethylenepentaamine (3,6,9-triazaundecane-1,11-diamine) by polarographic measurements at 25° at $I = 0.10$ (KCl) [17].

Due to hydrolysis, no stability constants are known for complexes of Tl^{3+} and Pb^{2+} with mono- and bidentate N-ligands. However, freshly precipitated $Tl(OH)_3$ is soluble in an aqueous penten solution, forming the 1:1 complex. A comparison of the data listed in *Table 1* shows that the formation of the penten complexes $[ML]^{n+}$ occurs stepwise as in the case with edta. For both, the more important species is $[MHL]^{(n+1)+}$, rather than $[ML]^{n+}$, in which all six N-donor-atoms are coordinated to the metal. Some steric strain is present as generally observed when several five-membered chelate rings are present simultaneously [5]. This could also signify that the metal ion may have already reached its highest coordination number. An example of this effect is represented by Cu^{2+} [4][5], because the spectral data for $CuHL^{3+}$ and CuL^{2+} are very similar (*Fig. 2*). Quite recently, it was shown that, in the solid state, $[Cu(penten)]^{2+}$ has a coordination number of five with a trigonal bipyramidal structure [18].

The metal ions Zn^{2+} and Co^{2+} provide other examples of this behavior. For these, the gain in the enthalpy of complex formation by coordination of the sixth N-donor is so low that, in solution, either all six N-atoms are weakly bound or that a mixture of penta- and hexa-coordinated penten complexes is present [4][5]. Only in the case of Mn^{2+}, the penten complex reaches a coordination number of seven with a coordinated H_2O molecule, as found for edta [5]. The highest pK values of the $[MHL]^{(n+1)+}$ species (p$K = \log \beta(MHL) - \log \beta(ML)$) are found for Ag^+ (9.34), followed by Hg^{2+} (8.46), Zn^{2+}(8.29), Cu^{2+} (8.05), Pb^{2+} (7.92), Mn^{2+} (7.74), Co^{2+} (7.43), Cd^{2+} (7.05), and Tl^{3+} (2.59).

One should note that the value of β for a given metal ion does not indicate the participation of a given N-atom to a particular chelate ring. In the case of Hg^{2+}, the coordination of the sixth N-atom is likely, given the high value of β, this in spite of the low tendency for MHL deprotonation. Similar considerations apply to the Hg-edta complex in the solid state [19].

In the case of Ag^+, one finds a diprotonated AgH_2L^{3+} species, which shows a low tendency for deprotonation (*Fig. 1*) and indicates that only four N-atoms might be bound. In contrast, the analogously less-stable PbH_2L^{4+} is a stronger acid with pK values 7.79 and 7.92, *vs.* 8.56 and 9.54 for $[AgH_2L]^{3+}$, in order to bind all six N-atoms in $Pb(penten)^{2+}$.

A comparison of the M−N distances in Tl³⁺-tpen and Tl³⁺-penten shows that the longest Tl−N bonds are found for N(21) and N(21a) of the central ethylenediamine unit (see *Table 3*). For the peripheral ligand N-atoms, the larger M−N distances are found for tpen, as one would expect due to the larger steric strain caused by the aromatic amine. As with the edta and tpen analogs [1][20], the space left free for further coordination in the absence of nitrate is *ca.* 43% of the coordination sphere, which shows the general preference of this cation for a coordination number larger than six. For the two hexaamines, it is unclear why NO_3^- in the tpen complex acts as a bidentate instead of monodentate ligand (as in the penten complex).

Table 3. *Crystallographic Data for [Tl(NO₃)(penten)](NO₃)₂*

Empirical formula	$C_{10}H_{28}N_9O_9Tl$
Formula weight [g mol⁻¹]	622.8
Crystallized from	H_2O
Crystal color, habit	Yellowish, cubic
Crystal dimensions [mm]	$0.1 \times 0.1 \times 0.1$
Temp. [K]	293
Crystal system	monoclinic
Space group	*P2/c*
Reflects. for cell determination	25
2θ Range for cell determ.	3 – 20
Unit cell parameters:	
a [Å]	13.141(2)
b [Å]	11.632(2)
c [Å]	12.955(2)
β [°]	93.22(1)
V [Å³]	1977.1(5)
Z	2
D_{calc} [g·cm⁻³]	2.092
$\mu(MoK_\alpha)$ (mm⁻¹)	8.234
$2\theta_{(max)}$ [°]	40
Absolute correction	Numeric
Transmission factors (min; max)	0.64, 0.79
Total reflections measured	3743
Symmetry-independent reflections	939
Reflections used [$F > 4\sigma(F)$]	928
Parameters refined	103
R	0.0395
wR	0.0556
Goodness-of-fit, s	1.53
Final Δ_{max}/σ	0.092
$\Delta\varrho$ (max; min) [e Å⁻³]	1.03, − 0.88
$\sigma(d(C-C))$ [Å]	0.05

Experimental Part

Safety Note. Thallium compounds are highly poisonous and should be handled with caution [21].

The nitrate salts of Mn^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, and Ag^+ (anal. grade, *Merck*) were dissolved in deionized, CO_2-free H_2O and standardized chelatometrically [22] or argentometrically [23]. The $Hg(ClO_4)_2$ soln. was prepared by dissolving HgO (*Merck*) in an excess of $HClO_4$. The Hg content was determined chelatometrically [23], and the excess acid was estimated by titration with strong base either by use of the *Gran* transformation [24] and/or from a non-linear regression. Anal. grade $NaNO_3$ and $NaClO_4 \cdot H_2O$ (*Merck*) were used as received.

The amine penten was synthesized as described in [1], and its purity was checked by ^{1}H- and ^{13}C-NMR spectroscopy and by alkalimetric titration. $[Tl(NO_3)(penten)](NO_3)_2$, synthesized by the method of *Musso* [20], gave an acceptable elemental analysis. The metal salt and ligand ($H_4penten^{4+}$) solns. were mixed, usually in a 1:1 molar ratio. In the case of Hg^{2+} and Tl^{3+}, excess strong acid was added. Sometimes, also chloride or bromide as auxiliary ligand was added. A total ionic strength of $I = 1.00$ was reached by addition of $NaNO_3$ (or $NaClO_4$ for Cu^{2+}, Hg^{2+}, and Tl^{3+}). These solns. were titrated with solns. containing 0.1M NaOH and 0.9M $NaNO_3$ (or $NaClO_4$ where appropriate).

Details regarding the measurements and calculation of stability constants are given in [25].

X-Ray Measurements. Determination of the Structure of [Tl(penten)NO₃](NO₃)₂. In a first step, the lattice parameters and the space group were determined with precession measurements. A second crystal was then used to check these parameters and to collect the data on a *SYNTEX P2₁* diffractometer with monochromated MoK_α radiation ($\lambda = 0.71073$ Å). The cell constants were calculated from the least-squares refinement of 25 well-centered reflections: $3° \leq 2\theta \leq 20°$. The stability of the crystal was checked by periodically recording three suitable orthogonal standard reflections. The crystals decompose under X-ray radiation, as evidenced by a change in color from yellowish to black. Upon a decrease in intensity of 20%, the crystal was replaced. The data sets were merged after correction for the respective intensity decrease.

The crystal data of $[Tl(NO_3)(penten)](NO_3)_2$ are given in *Table 3*. The determination of the structure was accomplished by the standard *Patterson* heavy-atoms method and *Fourier* synthesis with the *XTAL 3.2* program package [26] on a *CDC Cyber 855* system. The two nitrates, NO_3^-, were refined as rigid groups. The H-atoms were located in a subsequent difference-density map after isotropic refinement of the structure. The final refinement[2]) was accomplished with anisotropic displacement parameters for Tl, isotropic for all non-H atoms and with fixed isotropic displacement parameters and idealized positions for H-atoms.

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[2]) Crystallographic data (excluding structure factors) for the structure in *Fig. 3* reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC 144876. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44(1)1223-336033, e-mail: deposit@ccdc.cam.ac.uk).

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