

We also thank the reviewers for very helpful comments.

Registry No. I, 101224-80-0; II, 101224-81-1; [PEtPh₂Co((DO)(DOH)pn)CH₃]ClO₄, 101224-59-3; [P(EtCN)Ph₂Co((DO)(DOH)pn)CH₃]ClO₄, 101224-61-7; [P(OEt)Ph₂Co((DO)(DOH)pn)CH₃]ClO₄, 101224-63-9; [P(OMe)₂PhCo((DO)(DOH)pn)CH₃]ClO₄, 101224-65-1; [P(OMe)₃Co((DO)(DOH)pn)CH₃]ClO₄, 101224-66-2; [PPh₃Co((DO)(DOH)pn)CH₃]ClO₄, 101224-68-4; [P(Cy)Ph₂Co((DO)(DOH)pn)CH₃]ClO₄, 101224-70-8; [P(*i*-Pr)Ph₂Co((DO)(DOH)pn)CH₃]ClO₄, 101224-72-0; [P(4-Me₂NPh)₃Co((DO)(DOH)pn)CH₃]ClO₄, 101224-74-2; [P(Vi)Ph₂Co((DO)(DOH)pn)CH₃]ClO₄, 101224-76-4; [PBu₃Co

((DO)(DOH)pn)CH₃]ClO₄, 57385-47-4; [H₂OC₂Co((DO)(DOH)pn)CH₃]ClO₄, 23940-46-7; [(ANIL)Co((DO)(DOH)pn)CH₃]ClO₄, 101224-78-6; [H₂OC₂Co((DO)(DOH)pn)CH₃]PF₆, 101224-79-7.

Supplementary Material Available: Tables of elemental analyses, anisotropic thermal parameters, hydrogen atom coordinates, and complete bond lengths and bond angles (11 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors (26 pages) are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Complexes of Thallium(I) and -(III) Containing 1,4,7-Triazacyclononane (L) Ligands. Kinetics and Mechanism of the Reduction of [L₂Tl^{III}]³⁺. Crystal Structure of (N,N',N''-Trimethyl-1,4,7-triazacyclononane)thallium(I) Hexafluorophosphate

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Received October 28, 1985

The macrocycles 1,4,7-triazacyclononane (L), C₈H₁₅N₃, and N,N',N''-trimethyl-1,4,7-triazacyclononane (L'), C₉H₂₁N₃, reacted with TiCl₃·4H₂O (1:1) in chloroform, affording LTiCl₃ and L'TiCl₃, respectively. LTiI₃, L'TiI₃, and LTiBr₃ were prepared as orange-red solid materials. From a suspension of thallium(III) nitrate and 1,4,7-triazacyclononane (1:4) in chloroform colorless [TiL₂](NO₃)₃ was obtained. Thallium(I) nitrate reacted with N,N',N''-trimethyl-1,4,7-triazacyclononane in water to give upon addition of NaPF₆ or NaClO₄·H₂O the colorless salts L'Tl(PF₆) and L'Tl(ClO₄), respectively. The crystal structure of L'Tl(PF₆) has been determined by X-ray crystallography. Crystals of L'Tl(PF₆) belong to the orthorhombic space group *Pbca* with *a* = 11.77 (1) Å, *b* = 11.89 (1) Å, *c* = 23.19 (2) Å, *V* = 3245.3 Å³, and *Z* = 8. Least-squares refinement of the structure based on 1409 observations led to final discrepancy indices of *R* = 0.039. The structure consists of discrete L'Tl⁺ cations and PF₆⁻ anions. The lone pair of valence electrons of thallium(I) are considered to be stereochemically active in the solid. The kinetics of the reduction of [TiL₂]³⁺ with the strong one-electron reductant [Co^{II}L₂]²⁺ in aqueous solution (pH 7; *I* = 0.5 M (LiNO₃)) have been measured. The stoichiometry of the reaction has been determined: 2Co(II) + Ti(III) → 2Co(III) + Ti(I). A simple second-order rate law has been established for the formation of [Co^{III}L₂]³⁺ and TiL⁺ (*k* = 3.4 × 10⁻² M⁻¹ s⁻¹, 25 °C, *I* = 0.5 M). Outer-sphere one-electron transfer from Co(II) to Ti(III) with concomitant formation of a very reactive intermediate Ti(II) species is proposed to be the rate-determining step.

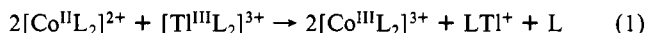
Introduction

In two papers we have shown that the small tridentate macrocycles 1,4,7-triazacyclononane (L) and N,N',N''-trimethyl-1,4,7-triazacyclononane (L') form stable complexes with the heavier main-group metals lead(II)² and indium(III)³ even in aqueous solution. The tridentate N-donor ligands coordinate facially in an octahedral ligand environment to these metal centers.

We here wish to report a series of such complexes containing the large thallium(I) and thallium(III) metal centers, respectively. Thallium porphyrin complexes have been investigated fairly extensively,⁴⁻⁷ but structural information on thallium compounds with saturated macrocyclic N-donor ligands is very scarce. Moras and Weiss⁸ have reported the X-ray structure of the thallium(I) cryptate (222), [(C₁₈H₃₆N₂O₆)Ti]HCOO·H₂O, Farago⁹ has reported thallium(I) complexes with macrocyclic crown polyethers, and Popov et al. have measured some stability constants of macrocyclic thallium(I) complexes,¹⁰ but no structural deter-

minations had been carried out. We have determined the crystal structure of L'Tl(PF₆), which contains L'Tl⁺ cations and non-coordinated PF₆⁻ anions. This complex appears to be the first example of a thallium(I) complex with a saturated N-donor ligand, which has been characterized by X-ray crystallography.

In addition, the preparation of [Ti^{III}L₂](ClO₄)₃ consisting of [Ti^{III}L₂]³⁺ cations, which are stable in aqueous solution, has prompted us to study the kinetics of its noncomplementary redox reaction with the strong outer-sphere one-electron-transfer reagent [Co^{II}L₂]²⁺ according to eq 1. The exact nature of reduced Ti(I) species has not been identified unambiguously.



Attempts to identify a thallium(II) intermediate species, which is proposed from the kinetic study, using normal and ultrafast cyclic voltammetry have failed.²⁸

Experimental Section

The ligands 1,4,7-triazacyclononane (L)^{11a} and N,N',N''-trimethyl-1,4,7-triazacyclononane (L')^{11b} have been prepared as described in the literature.

Preparation of Complexes. L'Tl(PF₆). A solution of thallium(I) nitrate (0.27 g; 1 mmol) and N,N',N''-trimethyl-1,4,7-triazacyclononane (0.18 g; 1 mmol) in water (50 mL) was heated to 90 °C for 30 min, after which time 0.4 g of potassium hexafluorophosphate was added. When the mixture was cooled to room temperature, a colorless solid precipitated, which was filtered off. X-ray-quality crystals were grown from a more dilute solution (300 mL of water) within 14 days at room temperature in an open vessel (yield 86%).

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Table I. Crystallographic Data (22 °C)

formula	(C ₉ H ₂₁ N ₃)Ti(PF ₆)
fw	520.6
space group	<i>Pbca</i> (<i>D</i> _{2h} ¹⁵)
<i>a</i> , Å	11.77 (1)
<i>b</i> , Å	11.89 (1)
<i>c</i> , Å	23.19 (2)
<i>V</i> , Å ³	3245.3
<i>Z</i>	8
<i>d</i> _{calcd.} , g cm ⁻³	2.131
cryst size, mm ³	0.17 × 0.47 × 0.63
μ _{Mo Kα} , cm ⁻¹	96.97
transmission factor (min-max)	0.15-1.00
data collecn instrum	AED II Siemens
radiation (graphite monochromated)	Mo Kα (λ = 0.71073 Å)
scan method	ω
data collecn range (2θ), deg	2.5-57
no. of reflns	1428
no. of unique data (<i>I</i> ≥ 1.5σ(<i>I</i>))	1409
no. of parameters refined	181
<i>R</i> , <i>R</i> _w	0.049, 0.039
GOF	2.06
max shift/esd (final cycle)	0.12
av shift/esd (final cycle)	0.03

A perchlorate salt, L'Tl(ClO₄), was obtained when sodium perchlorate monohydrate (0.5 g) was added to the above solution instead of KPF₆. Anal. Calcd for C₉H₂₁N₃TlPF₆: C, 10.84; H, 2.88; N, 6.32. Found: C, 10.8; H, 2.8; N, 6.3. Anal. Calcd for C₉H₂₁N₃TlClO₄: C, 22.7; H, 4.46; N, 8.86. Found: C, 22.5; H, 4.6; N, 8.8.

LTlCl₃ and L'TlCl₃. A suspension of thallium(III) chloride tetrahydrate (0.38 g, 1 mmol) and the respective cyclic amines L and L' (1 mmol) in chloroform (50 mL) was refluxed for 3 h. A colorless solid was filtered off, washed with ethanol and ether, and air-dried (yields ~90%).

Anal. Calcd for C₆H₁₅N₃TlCl₃: C, 16.42; H, 3.41; N, 9.63. Found: C, 16.8; H, 3.6; N, 9.5. Anal. Calcd for C₉H₂₁N₃TlCl₃: C, 22.41; H, 4.39; N, 8.70. Found: C, 22.4; H, 4.1; N, 8.7.

LTlBr₃. A solution of 1,4,7-triazacyclononane trihydrobromide (0.37 g; 1 mmol) in water (50 mL) was neutralized by dropwise addition of 2 M sodium hydroxide, and sodium bromide (10 g) was added with stirring. Upon addition of thallium(III) nitrate (0.39 g; 1 mmol) a colorless precipitate was formed, which redissolved on dropwise addition of 2 M NaOH. This solution was allowed to stand in an open vessel at room temperature. Within 3 days colorless crystals formed, which were filtered off, washed with ethanol and ether, and air-dried (yield 66%).

Anal. Calcd for C₆H₁₅N₃TlBr₃: C, 12.61; H, 2.63; N, 7.32. Found: C, 12.7; H, 2.6; N, 7.4.

LTlI₃ and L'TlI₃. LTlI₃ was prepared analogously to LTlBr₃ with use of sodium iodide (10 g) instead of NaBr. Small red-orange crystals were obtained (yield 63%).

L'TlI₃ was prepared from an aqueous solution (60 mL) of *N,N',N''*-trimethyl-1,4,7-triazacyclononane (1 mmol) and sodium iodide (10 g) to which thallium(III) nitrate (0.39 g, 1 mmol) was added with stirring at room temperature. A red precipitate was redissolved upon addition of a minimum amount of 2 M NaOH. Within 3 days in an open vessel at 20 °C red crystals formed, which were filtered off, washed with ethanol and ether, and air-dried (yield 56%).

Anal. Calcd for C₆H₁₅N₃TlI₃: C, 10.08; H, 2.11; N, 5.80; I, 53.29. Found: C, 10.2; H, 2.1; N, 5.9; I, 53.2. Anal. Calcd for C₉H₂₁N₃TlI₃: C, 13.05; H, 2.79; N, 5.01. Found: C, 13.1; H, 2.7; N, 4.9.

[L₂Tl](ClO₄)₃. A suspension of thallium(III) nitrate (0.39 g, 1 mmol) and 1,4,7-triazacyclononane (0.52 g; 4 mmol) in chloroform (50 mL) was refluxed for 24 h, after which time a colorless solid was filtered off and dissolved in 10⁻³ M sodium hydroxide (50 mL). Addition of sodium perchlorate monohydrate (0.5 g) initiated at room temperature the slow precipitation of colorless crystals, which were filtered off, washed with ethanol and ether, and air-dried (yield 50%).

Anal. Calcd for C₁₂H₃₀N₆Cl₃O₁₂Tl: C, 18.93; H, 3.97; N, 11.04; ClO₄, 39.19. Found: C, 18.8; H, 3.9; N, 10.9; ClO₄, 38.8.

X-ray Structure Determination. A colorless, tabular-shaped crystal of L'Tl(PF₆) was attached to the end of a glass fiber and mounted on an AED II Siemens diffractometer. Preliminary examinations showed that the crystal belonged to the orthorhombic system, space group *Pbca*. The unit cell dimensions (22 °C) were obtained by least-squares fit of the setting angles of 30 reflections. The data are summarized in Table I. Although the crystal used for data collection was of good size, the number of observed data is rather low due to a rapid falloff of high-angle ($\theta > 25^\circ$) reflection intensities. This effect accounts for the rather large estimated standard deviations of the unit cell parameters and the low

Table II. Atomic Coordinates (×10³) of L'Tl(PF₆)

atom	<i>x</i>	<i>y</i>	<i>z</i>
Tl	104.78 (6)	153.81 (5)	72.61 (3)
P	479.5 (5)	275.1 (4)	118.0 (3)
F1	592 (1)	324 (1)	143.6 (5)
F2	366 (1)	228 (1)	92.9 (6)
F3	537 (1)	230 (1)	63.5 (6)
F4	505 (2)	162 (1)	147.0 (6)
F5	420 (1)	313 (1)	174.5 (6)
F6	450 (1)	387 (1)	92.4 (7)
N1	391 (1)	182.2 (9)	403.4 (6)
N2	568 (1)	177 (1)	317.7 (6)
N3	561 (1)	365 (1)	401.1 (7)
C1	367 (2)	160 (2)	342 (1)
C2	460 (2)	126 (2)	307 (1)
C3	578 (2)	290 (2)	298 (1)
C4	605 (2)	375 (2)	340 (1)
C5	441 (1)	384 (1)	404 (1)
C6	365 (1)	298 (1)	422 (1)
C7	332 (2)	100 (1)	440 (1)
C8	653 (2)	106 (1)	288 (1)
C9	624 (2)	431 (1)	442 (1)

Table III. Selected Bond Distances (Å) and Angles (deg) of L'Tl(PF₆)

Tl-N1	2.60 (1)	C1-C2	1.43 (3)
Tl-N2	2.59 (2)	C3-C4	1.43 (3)
Tl-N3	2.63 (1)	C5-C6	1.42 (3)
Tl-F2	3.23 (1)	N2-C3	1.43 (3)
Tl-F3	3.54 (2)	N2-C2	1.43 (3)
Tl-F6	3.27 (1)	N2-C8	1.48 (2)
P-F1	1.56 (1)	N1-C1	1.48 (2)
P-F2	1.56 (1)	N1-C6	1.47 (2)
P-F3	1.53 (1)	N1-C7	1.46 (2)
P-F4	1.53 (1)	N3-C4	1.52 (3)
P-F5	1.56 (1)	N3-C5	1.43 (2)
P-F6	1.50 (1)	N3-C9	1.43 (2)
N1-Tl-N2	67.4 (6)	N3-Tl-F3	78.0 (5)
N1-Tl-N3	68.7 (4)	N3-Tl-F2	83.9 (5)
N2-Tl-N3	68.9 (5)	N2-Tl-F2	89.3 (6)
F2-Tl-F3	103.9 (6)	N2-Tl-F6	86.0 (6)
F2-Tl-F6	115.4 (6)	N1-Tl-F6	84.6 (5)
F3-Tl-F6	117.3 (7)	N1-Tl-F3	85.5 (6)

ratio of data/parameters. Intensity data were measured by 22 °C by ω scans and were corrected for Lorentz and polarization effects. An empirical absorption correction was carried out.¹² The structure was solved via Patterson and Fourier syntheses. Idealized positions of the methylene H atoms were calculated and included in the refinement cycles with isotropic thermal parameters. The function minimized during least-squares refinements was $\sum w(|F_o| - |F_c|)^2$ with final convergence factors $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ and $w = 1/\sigma^2(F)$. Scattering factors for all atoms were taken from ref 13. The real and imaginary parts of anomalous dispersion for all non-hydrogen atoms were included.¹³ The final atomic parameters are given in Table II and bond distances and angles in Table III. A list of observed and calculated structure factors, a table of anisotropic thermal parameters of all non-hydrogen atoms, and a table of calculated positional parameters of hydrogen atoms are available as supplementary material.

Kinetic Measurements. Solutions containing [Co^{III}L₂]²⁺ were prepared from aqueous solutions of [Co^{III}L₂]Cl₃ and zinc amalgam as reductant under an argon atmosphere. Freshly prepared solutions were injected into argon-scrubbed solutions containing [TlL₂](ClO₄)₃. The ionic strength was adjusted to 0.5 M with lithium nitrate as electrolyte. Due to solubility problems of [TlL₂](ClO₄)₃, lithium perchlorate could not be used. Lithium chloride or lithium bromide proved also to be unsuitable for the adjustment of ionic strength due to precipitation of thallium(I) chloride or thallium(I) bromide during the course of the reaction. The formation of [Co^{III}L₂]³⁺ was monitored as a function of time using conventional

(12) Computations were carried out on an Eclipse computer using the program package STRUCSY ("Structure Computation System"; Stoe: Darmstadt, FRG).

(13) *International Tables of X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

spectrophotometry. A Unicam SP 1700 spectrophotometer interfaced to a Commodore VC 64 computer was used for data acquisition and analysis. All reactions were run under pseudo-first-order conditions (excess CoL_2^{2+}) under an argon atmosphere. Pseudo-first-order rate constants were calculated with a least-squares program¹⁴ where the absorptions at the beginning ($t = 0$) and after the completed reaction ($t = \infty$) were treated as variables. The observed and calculated values differed only within the uncertainty of the last digit of the readings of the instrument.

Results and Discussion

Preparation of Complexes. The reaction of the macrocycles 1,4,7-triazacyclononane and N,N',N'' -trimethyl-1,4,7-triazacyclononane with thallium(III) chloride tetrahydrate in the ratio 1:1 in chloroform yields colorless solid materials of the composition LTiCl_3 and L'TiCl_3 . The analogous complexes LTiI_3 and L'TiI_3 were prepared from aqueous solution containing thallium(III) nitrate, the respective macrocycle (1:1), and sodium iodide. Orange-red solids precipitated. LTiBr_3 was prepared analogously. These LTiX_3 and L'TiX_3 complexes ($X = \text{Cl}, \text{Br}, \text{I}$) are insoluble in water and nonpolar organic solvents. Since the macrocyclic ligands coordinate facially to an octahedron only, the structure of these complexes is proposed to be *fac*- LTiX_3 . Many complexes of thallium(III) of type $\text{TiX}_3(\text{N-donor})_3$, where X represents halide and the N-donors are monodentate ligands such as pyridine (py), pyrazine, and quinoline, are known.¹⁵ $\text{TiCl}_3(\text{py})_3$ has been shown by X-ray crystallography to consist of the octahedral, neutral species *mer*- $\text{TiCl}_3(\text{py})_3$.

The reaction of 1,4,7-triazacyclononane with thallium(III) nitrate (4:1) in refluxing chloroform yields a colorless solid, which readily dissolves in water. Addition of sodium perchlorate hydrate initiates the rapid precipitation of $[\text{L}_2\text{Ti}](\text{ClO}_4)_3$. Aqueous solutions of this salt are quite stable for at least 6 h at room temperature. No indications of ligand dissociation have been observed during this time. Crystals of $[\text{L}_2\text{Ti}](\text{ClO}_4)_3$ proved to be unsuitable for a complete X-ray structure determination of high precision. But even from an incomplete analysis the molecular structure of the $[\text{L}_2\text{Ti}]^{3+}$ group was clearly established.¹⁷ Two tridentate macrocycles are coordinated to a thallium(III) center in a distorted-octahedral fashion. The average Ti-N bond distance is 2.48 (2) Å, which agrees well with Ti-N bond distances found in $\text{TiBr}_3(\text{C}_5\text{H}_5\text{N})_2$ ¹⁸ and $\text{TiCl}_3(\text{phen})$ ¹⁹ (phen = 1,10-phenanthroline). Thallium(III) complexes containing an octahedral N_6 -donor set are known, e.g. $[\text{Ti}(\text{en})_3]\text{Cl}_3 \cdot 3\text{H}_2\text{O}$ ²⁰ and $[\text{Ti}(\text{bpy})_3]\text{X}_3$ ²¹ (en = ethylenediamine; bpy = 2,2'-bipyridine), although no X-ray crystal structure determinations appear to have been carried out.

Thallium(I) nitrate reacts with N,N',N'' -trimethyl-1,4,7-triazacyclononane in aqueous solution to form a 1:1 complex, which has been isolated as the hexafluorophosphate and perchlorate salts by addition of sodium hexafluorophosphate and sodium perchlorate hydrate, respectively. The crystal structure of $\text{L'Ti}(\text{PF}_6)$ has been determined (see below). The stability of the L'Ti^+ cation in aqueous solution is not very great, since addition of chloride or bromide ions initiates the rapid precipitation of TiCl and TiBr , respectively.

Description of the Crystal Structure of $\text{L'Ti}(\text{PF}_6)$. Crystals of $\text{L'Ti}(\text{PF}_6)$ consist of L'Ti^+ cations and PF_6^- anions. Figure 1 shows

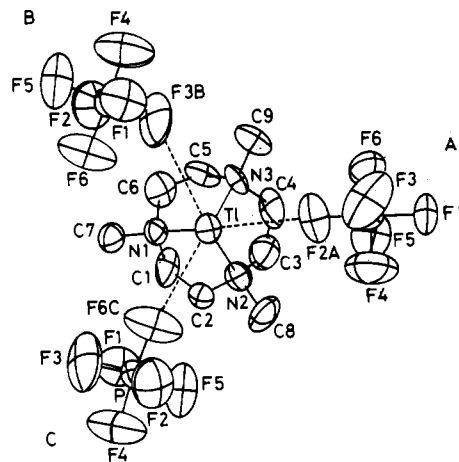


Figure 1. Perspective view of $\text{L'Ti}(\text{PF}_6)$ and atomic labeling scheme. The environment of the L'Ti^+ moiety surrounded by PF_6^- anions is emphasized. Broken lines indicate nonbonded interactions between Ti and F.

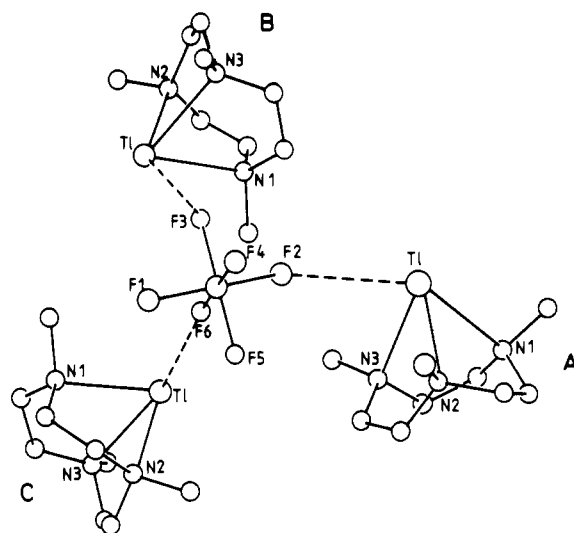


Figure 2. Perspective view of $\text{L'Ti}(\text{PF}_6)$ emphasizing the environment of one PF_6^- anion surrounded by three L'Ti^+ moieties. Broken lines indicate nearest nonbonding distances between Ti and F.

a perspective view of the L'Ti^+ cation and its nearest three PF_6^- neighbors and the atomic labeling scheme. In Figure 2 the environment of one PF_6^- group is emphasized. Each L'Ti^+ unit is surrounded by three PF_6^- groups, and each PF_6^- unit has three L'Ti^+ units as nearest neighbors.

The L'Ti^+ moiety consists of a thallium(I) center and a tridentate N,N',N'' -trimethyl-1,4,7-triazacyclononane ligand. The average Ti-N bond distance is 2.61 (1) Å. The sum of the ionic radii of thallium(I) (coordination number 6) and nitrogen (coordination number 4) is 2.96 Å.²² Therefore, the Ti-N bonds in L'Ti display considerable covalent character. In $[(\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6)\text{Ti}]\text{HCOO} \cdot \text{H}_2\text{O}$, the only other well-characterized compound of thallium(I) containing a saturated N donor, the Ti-N bond distance is 2.946 (6) Å, indicating that these bonds are electrostatic in character.⁸ The average N-Ti-N bond angles are much smaller than 90° (68°), which is due to the steric constraints of the cyclononane ring and the long Ti-N bond distances. The L'Ti^+ cation has very similar geometry as has been found in LPbX_2 ($X = \text{NO}_3^-, \text{ClO}_4^-, \text{Br}^-$).²

In solid $\text{L'Ti}(\text{PF}_6)$ each L'Ti^+ unit is surrounded by three fluorine atoms of different PF_6^- anions (Figure 1). These Ti...F distances range from 3.23 (1) to 3.54 (2) Å. The sum of the ionic radii of Ti(I) and F^- is 2.79 Å,²² and the sum of the atomic radii

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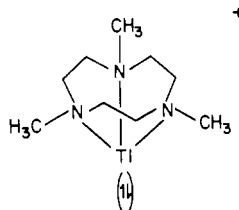
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Table IV. Kinetic Data for the Reduction of $[\text{TlL}_2]^{3+}$ by $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$ in Aqueous Solution^a

$T, ^\circ\text{C}$	$[\text{Co}(\text{II})], \text{M}$	$10^3 k_{\text{obsd}}, \text{s}^{-1}$	$T, ^\circ\text{C}$	$[\text{Co}(\text{II})], \text{M}$	$10^3 k_{\text{obsd}}, \text{s}^{-1}$
15	0.05	1.51	25	0.02	1.54
	0.035	0.92		0.01	0.675
	0.02	0.53	35	0.035	6.32
	0.01	0.32		0.02	3.36
25	0.05	3.5	0.01	2.37	
	0.035	2.24			

^a Conditions: $I = 0.5 \text{ M}$ (LiNO_3); $[\text{TlL}_2^{3+}] = 1.0 \times 10^{-3} \text{ M}$.

(van der Waals radii) is 3.50 \AA .²³ Therefore, the Tl-F distances found in $\text{L}'\text{Tl}(\text{PF}_6)$ are essentially nonbonding with only very weak ionic character. It is nevertheless instructive to consider the TlN_3F_3 polyhedron. The F-Tl-F angles range from 104 to 117.3° , whereas the N-Tl-N angles are much smaller than 90° (average $\sim 68.4^\circ$) and the N-Tl-F angles are also smaller than 90° . The nonbonding F...F distances in the TlN_3F_3 polyhedron are significantly larger than they would be if the F-Tl-F angles were the usual octahedral angle of 90° . This may be an indication that the stereochemically active lone pair of valence electrons of the thallium(I) is directed toward the center of the F_3 face in the TlN_3F_3 distorted octahedron:



Very similar evidence has been presented for the LPb^{2+} moiety.²

The PF_6^- anions have a regular octahedral geometry with an average P-F bond distance of 1.54 \AA . Three fluorine atoms of a PF_6^- anion, which are cis positions with respect to each other, are nearest neighbors to three different $\text{L}'\text{Tl}^+$ cations (Figure 2).

Kinetics and Mechanism of the Reduction of $[\text{Tl}^{\text{III}}\text{L}_2]^{3+}$ by $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$. The cation $[\text{TlL}_2]^{3+}$ is stable in water for at least 6 h at ambient temperature. No indication of ligand dissociation was detected. Even in slightly alkaline solutions of $[\text{TlL}_2](\text{ClO}_4)_3$ (pH 8–9) no precipitation of $\text{Tl}(\text{OH})_3$ has been observed; addition of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ to such solutions led to nearly quantitative recovery of solid $[\text{TlL}_2](\text{ClO}_4)_3$. $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$ and $[\text{Co}^{\text{III}}\text{L}_2]^{3+}$ are also stable toward ligand dissociation under these conditions.²⁴

The stoichiometry of the reduction of $[\text{Tl}^{\text{III}}\text{L}_2]^{3+}$ by $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$ in aqueous solution was determined spectrophotometrically by monitoring the amount of $[\text{Co}^{\text{III}}\text{L}_2]^{3+}$ produced using excess $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$ over a known amount of $[\text{TlL}_2]^{3+}$ (eq 1). Upon reduction of one $[\text{TlL}_2]^{3+}$ ion two $[\text{Co}^{\text{III}}\text{L}_2]^{3+}$ ions are produced; the reaction is a noncomplementary redox reaction.

Evidence for the formation of $[\text{Tl}]^+$ is only circumstantial since we have not been able to isolate a crystalline salt containing this cation. On the other hand, the preparation and isolation of the analogous TlClO_4 salt (see above) demonstrates the possibility of the formation of such species. Complete hydrolysis to $\text{Tl}(\text{OH})_3$ during the reaction cannot be ruled out.

The kinetics of the reduction were studied at pH 7 with use of pseudo-first-order conditions with $[\text{Co}^{\text{II}}]$ in large excess over $[\text{Tl}(\text{III})]$ ($1 \times 10^{-3} \text{ M}$) and an ionic strength of 0.5 M (LiNO_3). The increase in absorbance at $\lambda = 458 \text{ nm}$ (formation of $[\text{Co}^{\text{III}}\text{L}_2]^{3+}$) was followed spectrophotometrically as a function of time. The observed pseudo-first-order rate constants showed a linear dependence on $[\text{Co}^{\text{II}}\text{L}_2]$ (Figure 3 and Table IV); a simple second-order rate law has been established (eq 2) for reaction 1.

$$d[\text{Co}^{\text{III}}]/dt = 2k[\text{Tl}^{\text{III}}][\text{Co}^{\text{II}}] \quad (2)$$

Second-order rate constants at 15, 25, and 34°C were evaluated

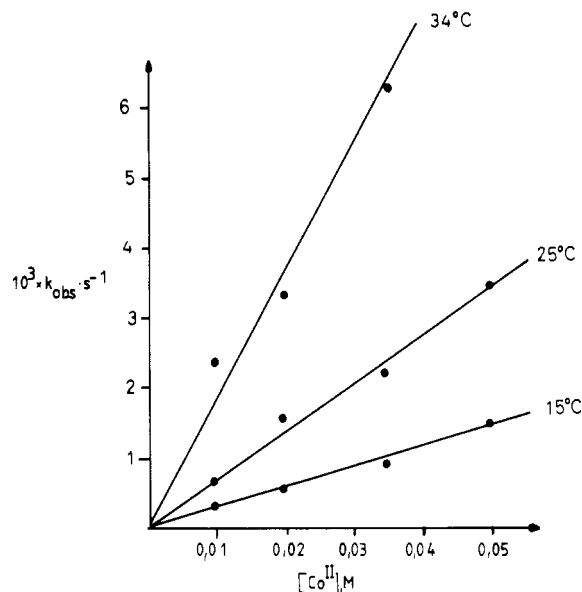


Figure 3. Plot of $k_{\text{obsd}} (\text{s}^{-1})$ vs. $[\text{Co}(\text{II})] (\text{M})$ for the reaction between $[\text{L}_2\text{Tl}]^{3+}$ and $[\text{CoL}_2]^{2+}$ ($I = 0.5 \text{ M}$ (LiNO_3); $[\text{L}_2\text{Tl}^{3+}] = 1.0 \times 10^{-3} \text{ M}$).

with use of a least-squares program to be 1.45×10^{-2} , 3.4×10^{-2} , and $0.085 \text{ M}^{-1} \text{ s}^{-1}$, respectively. Activation parameters are $\Delta H^\ddagger = 16 \pm 1 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -11 \pm 4 \text{ cal K}^{-1} \text{ mol}^{-1}$.

Since $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$ is a strong one-electron outer-sphere reductant ($E_{1/2}$ of the couple $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$ is -0.40 V vs. NHE^{24}), $[\text{Tl}^{\text{III}}\text{L}_2]^{3+}$ must be reduced in the rate-determining step by an outer-sphere one-electron transfer.²⁹ It should be noted that $[\text{TlL}_2]^{3+}$ is also an inert hexacoordinate species with no additional labile coordination sites and, therefore, it can only be reduced via an outer-sphere electron-transfer process. This implies the formation of a reactive intermediate species of thallium(II), which is reduced to thallium(I) in a very rapid successive step by a second $[\text{Co}^{\text{II}}\text{L}_2]^{2+}$ ion.²⁹ This behavior of $[\text{Tl}^{\text{III}}\text{L}_2]^{3+}$ acting as a strictly one-electron oxidant is in contrast to the redox chemistry of $\text{Tl}_{\text{aq}}^{3+}$, which is believed to function as a two-electron acceptor in a single step in some instances.^{25–27} This requires an inner-sphere-type activated complex between $\text{Tl}_{\text{aq}}^{3+}$ and the reductant. This type of activated complex is precluded in the present reaction due to the coordination of both metal centers involved to two 1,4,7-triazacyclononane ligands, respectively. Since the redox potential of the couple $[\text{TlL}_2]^{3+/2+}$ is not known, we cannot comment on the $\text{Tl}(\text{III}/\text{II})$ self-exchange rate or give an estimate using the Marcus cross relation.

Attempts to identify the proposed $[\text{Tl}^{\text{II}}\text{L}_2]^{2+}$ intermediate electrochemically have failed. Cyclic voltammograms of $[\text{TlL}_2](\text{ClO}_4)_3$ in aqueous and acetonitrile solutions at a mercury electrode at normal (100 mV s^{-1}) and ultrafast scan rates (1000 V s^{-1}) indicate an irreversible three-electron process producing thallium metal. At gold electrodes an irreversible two-electron reduction was accomplished and at more negative potentials thallium metal was deposited at the electrode.²⁸ The rapid loss of one coordinated ligand L in the proposed $[\text{TlL}_2]^{2+}$ intermediate may be the reason for this irreversible electrochemical behavior.

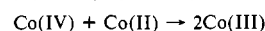
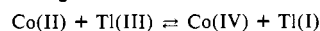
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we feel that this is not very likely since in the potential range -1.0 to $+1.2 \text{ V}$ vs. NHE no indication for an oxidation of $[\text{CoL}_2]^{3+}$ had been found²⁴ and an outer-sphere two-electron transfer in the rate-determining step is an improbable event.

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Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support of this work.

Registry No. L/Tl(PF₆), 101165-02-0; L/Tl(ClO₄), 101165-03-1; LTlCl₃, 101165-04-2; L/TlCl₃, 101165-05-3; LTlBr₃, 101165-06-4; LTlI₃, 101165-07-5; L/TlI₃, 101165-08-6; [L₂Tl](ClO₄)₃, 101165-10-0; CoL₂²⁺, 91760-59-7.

Supplementary Material Available: Tables of anisotropic thermal parameters, calculated positional parameters of H atoms, and bond angles (3 pages). Ordering information is given on any current masthead page. According to policy instituted Jan 1, 1986, the tables of calculated and observed structure factors are being retained in the editorial office for a period of 1 year following the appearance of this work in print. Inquiries for copies of these materials should be directed to the Editor.

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Complex Formation between Cu²⁺ and 1,N⁶-Ethenoadenosine 5'-Triphosphate (ε-ATP)

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Received December 18, 1985

By potentiometric pH titrations and UV spectrophotometric measurements the complexes formed in the Cu²⁺/ε-ATP 1:1 system are characterized in the pH range 3.4-8. The main species occurring are Cu(H·ε-ATP)⁻, Cu(ε-ATP)²⁻, and Cu₂H(ε-ATP)₂³⁻; this contrasts with the Cu²⁺/ATP system where Cu(H·ATP)⁻ and Cu(ATP)²⁻ are dominating. Due to the intense back-binding to the N-6/N-7 site of the 1,N⁶-ethenoadenine residue, the stability of Cu(ε-ATP)²⁻ is much larger (log K^{Cu}_{Cu(ε-ATP)} = 9 ± 1) than that of Cu(ATP)²⁻ (log K^{Cu}_{Cu(ATP)} = 6.32 ± 0.04). Consequently, the extent of macrochelate formation (i.e., simultaneous coordination of Cu²⁺ to the phosphate chain and the base residue) reaches with Cu(ε-ATP)²⁻ more than 99.5%, while for Cu(ATP)²⁻ this "closed" species involving N-7 occurs only to about 70%. As a result of these differences one must conclude that ε-ATP should never be employed as a probe for ATP in the presence of Cu²⁺.

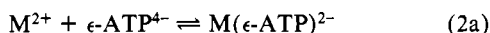
Adenosine 5'-triphosphate (ATP⁴⁻) is in nature a widely used substrate for many enzymic reactions, and there are indications that Cu(ATP)²⁻ might be a natural active form of Cu²⁺.¹ As ε-ATP is a popular probe for ATP (Chart I),² mainly due to its fluorescent qualities, we studied the properties of the Cu²⁺/ε-ATP system in aqueous solution. The results show that the stabilities and structures of the Cu²⁺/ε-ATP complexes differ so much from those of Cu²⁺/ATP that ε-ATP should never be employed as a probe for ATP in the presence of Cu²⁺.

Results and Discussion

The experimental data³ from potentiometric pH titrations of Cu²⁺/ε-ATP cannot be explained by the sole formation of Cu(H·ε-ATP)⁻ and Cu(ε-ATP)²⁻. This contrasts with the Mg²⁺, Mn²⁺, and Zn²⁺/ε-ATP systems⁴ where the data could well be accounted for with H⁺, H₂(ε-ATP)²⁻, H(ε-ATP)³⁻, ε-ATP⁴⁻, M²⁺, M(H·ε-ATP)⁻, and M(ε-ATP)²⁻, i.e., by considering the following two equilibria:



$$K_{M(H\cdot\epsilon\text{-ATP})}^M = [M(H\cdot\epsilon\text{-ATP})^{-}] / ([M^{2+}][H(\epsilon\text{-ATP})^{3-}]) \quad (1b)$$



$$K_{M(\epsilon\text{-ATP})}^M = [M(\epsilon\text{-ATP})^{2-}] / ([M^{2+}][\epsilon\text{-ATP}^{4-}]) \quad (2b)$$

The acidity constant of the connected equilibrium 3 is calculated with eq 4.

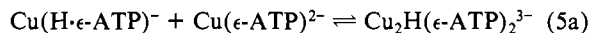


$$K_{M(H\cdot\epsilon\text{-ATP})}^H = [M(\epsilon\text{-ATP})^{2-}][H^{+}] / [M(H\cdot\epsilon\text{-ATP})^{-}] \quad (3b)$$

$$pK_{M(H\cdot\epsilon\text{-ATP})}^H = pK_{H(\epsilon\text{-ATP})}^H + \log K_{M(H\cdot\epsilon\text{-ATP})}^M - \log K_{M(\epsilon\text{-ATP})}^M \quad (4)$$

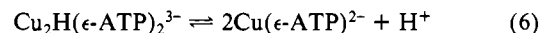
The spectrophotometric results shown in the upper part of Figure 1 also suggest that in the Cu²⁺/ε-ATP system additional complex species are formed: considering the dependence of the absorption at 260 or 271 nm on pH it is evident that the absorption decreases to a minimum at about pH 4.5 and rises then again. Hence, at least one further complex must be formed. These observations are also quite different from those made for the Zn²⁺/ε-ATP system.⁴

1. Estimation of Equilibrium Constants. As the titration data indicated a first inflection point after liberation of "half a proton" per ligand molecule besides the final equivalence point, we assumed that a complex Cu₂H(ε-ATP)₂³⁻ might be formed according to the dimerization equilibrium 5. This species would liberate "half



$$K_{D/Cu,\epsilon\text{-ATP}} = [Cu_2H(\epsilon\text{-ATP})_2^{3-}] / ([Cu(H\cdot\epsilon\text{-ATP})^{-}][Cu(\epsilon\text{-ATP})^{2-}]) \quad (5b)$$

a proton" via process 6. A first attempt to fit the experimental



data, on the basis of the model containing the complexes Cu(H·ε-ATP)⁻, Cu(ε-ATP)²⁻, and Cu₂H(ε-ATP)₂³⁻ [aside from H₂(ε-ATP)²⁻, H(ε-ATP)³⁻, and ε-ATP⁴⁻] by using the program TITFIT⁸ failed. The iterative process did not converge, because titration data were available only at pH > 3.4, and here the complex Cu(H·ε-ATP)⁻ is already fully formed. Hence, in a series of calculations the value for log K^{Cu}_{Cu(ε-ATP)} was kept constant and now the iteration converged readily. The corresponding results are listed in Table I.

From preliminary calculations it became immediately clear that log K^{Cu}_{Cu(ε-ATP)} > 8 (Table I): with log K^{Cu}_{Cu(ε-ATP)} = 8.0 the standard deviation between the experimental and calculated

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(3) Equipment, materials, and experimental procedures were the same as given in ref 4. Three independent titrations with 1 mL of 0.04 M NaOH were carried out for aqueous solutions with [Cu²⁺] = [ε-ATP⁴⁻] = 0.288, 0.336, and 0.384 mM (volume 50 mL) in the presence of 0.72 mM HNO₃ and NaNO₃ (I = 0.1; 25 °C). In these concentrations self-stacking of ε-ATP is negligible.⁵ The experiments were also done such that dephosphorylation of ε-ATP, which is metal ion promoted⁶ like that of other nucleoside 5'-triphosphates,⁷ was kept to a minimum.

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