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Formation and structure of novel ternary complexes of thallium(III)-cyanide–amine (ethylenediamine and triethylenetetramine) in solution and in solid

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Abstract

A novel ternary Tl(III) complex $[\text{Tl}(\text{en})_2(\text{CN})]^{2+}$ has been synthesized and characterized in solution by NMR and in solid by Raman spectroscopy. This complex has been prepared in the solid state, $[\text{Tl}(\text{en})_2(\text{CN})](\text{ClO}_4)_2$ (**1**), and the related $[\text{Tl}(\text{tren})(\text{CN})_2](\text{ClO}_4)_2$ (**2**), and their crystal structures determined by X-ray diffraction. A linear cyano-bridged supramolecular complex exists in $[\text{Tl}(\text{en})_2(\text{CN})](\text{ClO}_4)_2$. In $[\text{Tl}(\text{tren})(\text{CN})_2](\text{ClO}_4)_2$, the thallium ion exists in a distorted octahedral geometry *cis* coordinated cyanides.

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Keywords: Thallium; Cyano bridge; Ethylenediamine; Triethylenetetramine; Multinuclear NMR; Ternary complexes

1. Introduction

Studies of Tl(III) complexes with organic nitrogen donor ligands in aqueous solution are difficult due to the strongly hydrolytic and oxidative properties of this metal ion. The binary systems of Tl(III) with chloride and bromide have been studied [1,2]. Recently, the formation and equilibria of $[\text{Tl}(\text{CN})_n]^{3-n}$ ($n = 1-4$) [3,4] and $[\text{Tl}(\text{en})_n]^{3+}$ ($n = 1-3$) [5] complexes have been investigated in solution by means of ²⁰⁵Tl and ¹³C NMR. They indicated that Tl(III) formed very stable complexes both with the ‘soft’ cyanide ligands and with the ‘harder’ N-donor ligand ethylenediamine. In a ternary system, only the complex formation for Tl(III)–CN[−]–Cl[−] has been studied [6]. The coordina-

tion geometry of Tl(III) is quite versatile and varies depending on the ligand, e.g. it is tetrahedral in $[\text{Tl}(\text{CN})_4]^-$ [3] and in $[\text{TlI}_4]^-$ [7–9], octahedral in $[\text{Tl}(\text{en})_3]^{3+}$ [5], $[\text{Tl}(\text{H}_2\text{O})_6]^{3+}$ [10] and in $[\text{TlCl}_5(\text{dmsO})]^{2-}$ [11], seven-coordinated in $[\text{Tl}(\text{edta})(\text{OH})]^{2-}$ [12], $[\text{Tl}(\text{edta})(\text{CN})]^{2+}$ [13] and $[\text{Tl}(\text{bipy})_3(\text{dmsO})]^{3+}$ [14], and eight coordinated in $[\text{Tl}(\text{bipy})_2(\text{NO}_3)_3]$ [12], $\{\text{C}(\text{NH}_2)_3\}_3[\text{Tl}(\text{Nta})_2] \cdot (2\text{H}_2\text{O})$ and $\text{Ti}_3[\text{Tl}^{\text{III}}(\text{Nta})_2]$ [15]. We have previously studied complexes of Tl(III)–en in pyridine [5] and of Tl(III)–CN[−] in aqueous solution [4]. Here, we report the synthesis and NMR characterization of the ternary $[\text{Tl}(\text{en})_2(\text{CN})]^{2+}$ complex in aqueous solution and the crystal structures of $[\text{Tl}(\text{en})_2(\text{CN})](\text{ClO}_4)_2$ and $[\text{Tl}(\text{tren})(\text{CN})_2](\text{ClO}_4)_2$ in the solid state.

2. Experimental

2.1. Preparation

The reagents were all of analytical grade. The stock solution of concentrated acidic $\text{Tl}(\text{ClO}_4)_3$ was prepared by anodic oxidation of TlClO_4 [16a,16b]. The concen-

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trations of Tl(III) and HClO_4 were determined by the titration with 0.1 M standard NaOH and KBrO after adding excess of solid NaCl to the analyzed solution using methyl orange as indicator [16c].

2.1.1. Synthesis

2.1.1.1. Compound 1. A mixture of 0.03 g of NaCN (0.6 mmol) and 0.166 ml solution of 1.2 M $\text{Tl}(\text{ClO}_4)_3$ (0.2 mmol) containing 5 M HClO_4 was dissolved in 2 ml water. A 20 μl aliquot of neat ethylenediamine ($\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2\cdot\text{H}_2\text{O}$) (0.267 mmol) was added (pH 2.5). When the solution was stored in a closed flask in a refrigerator, white cube-shaped crystals were formed.

2.1.1.2. Compound 2. A mixture of 0.03 g of NaCN (0.6 mmol) and 0.166 ml solution of 1.2 M $\text{Tl}(\text{ClO}_4)_3$ (0.2 mmol) containing 5 M HClO_4 were dissolved in 2 ml water. Then, 75 μl (0.3 mmol) of a 60% solution of triethylenetetramine ($\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2-\text{NH}_2$) was added. Then the solution was stored in a closed flask in a refrigerator; white cube-shaped crystals were formed in the bottom of the flask. Raman spectra of the compounds were recorded with a Renishaw System 1000 spectrometer equipped with a Leica DMLM microscope, a 25 mW diode laser (780 nm), and a Peltier-cooled CCD detector. The band positions and assignment are as follows: compound **1**: 2955w, 2893w (NH_2 and CH_2 str.); 2148s ($\text{C}\equiv\text{N}$ str.); 1589m, 1460m, 1395m, 1283m (CH_2 and NH_2 bend); 1143m, 1021m (CN and CC str.); 931vs, 625s (ClO_4^- str.); 460s (TIC of $\text{C}\equiv\text{N}$ str.); 437vs, 321s (TIN of NH_2 str.); compound **2**: 2956w, 2892w (NH_2 and CH_2 str.); 2156s ($\text{C}\equiv\text{N}$ str.); 1593w, 1470m, 1456m, 1388w, 1364w 1260m (CH_2 and NH_2 bend); 1094m, 991m (CN and CC str.); 930vs, 616s (ClO_4^- str.); 467s (TIC of $\text{C}\equiv\text{N}$ str.); 417vs, 345s (TIN of NH_2 str.). The abbreviations are: vs, very strong; s, strong; m, medium; w, weak.

2.2. NMR measurements

All NMR spectra were recorded with a Bruker DMX-500 MHz spectrometer at a probe temperature of 25 (\pm 0.5) $^\circ\text{C}$. NMR parameters were chosen in order to obtain quantitative spectra.

2.3. ^{205}Tl NMR

Spectrometer frequency (SF) = 288.5 MHz; spectral window (SW) = 23–86.5 kHz; flip angle approximately 45° ; pulse repetition time approximately 0.5–1.0 s; number of scans (NS) = 500. The chemical shift values are referred in ppm toward higher frequency from the ^{205}Tl NMR signal of an aqueous solution of TlClO_4 extrapolated to infinite dilution.

2.4. ^{13}C NMR

^{13}C NMR spectra were recorded at SF = 125.7 MHz with typical NMR parameters: flip angle approximately 30° ; spectral window = 25.1 kHz; pulse repetition time = 3.5 s; proton decoupled. The chemical shifts are accurate within ± 0.1 ppm and are reported in ppm with respect to external TMS.

2.5. X-ray crystallography

An irregular crystal of **1**, approximately $0.03 \times 0.03 \times 0.1$ mm, enclosed in a thin-walled glass capillary was used for data collection. The data collection was performed on an Enraf–Nonius CAD4 diffractometer using λ (Mo $\text{K}\alpha$, 0.71073 Å) radiation with a graphite monochromator. After 6 h of measurement, the crystal decomposed. The intensity of the reference reflections decreased by a factor of 5 (the width of the reflections increased by four times), which was taken into account in the data processing. The structure was solved by the heavy-atom method. Hydrogen atoms in the structure were calculated from geometric considerations. The SHELXTLPLUS (PC version) program package was used for all calculations.

The data of **2** were collected on a Nonius–Kappa CCD area detector, λ (Mo $\text{K}\alpha$) = 0.71073 Å, using a graphite monochromator. Numerical absorption correction was applied [17]. The structure was solved by direct methods [18] and refined using full-matrix least-squares on F^2 (SHELXL-97) [19]. All the non-hydrogen atoms in compounds **1** and **2** were refined with anisotropic displacement parameters. Selected crystal data and parameters of **1** and **2** are listed in Table 2.

3. Results and discussion

3.1. NMR characterization in solution

^1H , ^{13}C and ^{205}Tl NMR spectra have been recorded for an aqueous solution with the molar ratio $\text{Tl(III)}:\text{CN}^-:\text{en} = 1:3:1.2$ (pH 2.5). The data are listed in Table 1. The proton decoupled ^{13}C spectrum (25% enriched ^{13}CN was used) is shown in Fig. 1. There are three sharp singlet signals: the one at 115.0 ppm belongs to the protonated cyanide (HCN) and the other two at 41.7 and 39.7 ppm, respectively, belong to the free and coordinated ethylenediamine; the two 1:1 doublet signals centered at 142.2 and 147.1 ppm originate from two Tl(III) cyanide species, $[\text{Tl}(\text{CN})]^{2+}$ and $[\text{Tl}(\text{en})_2(\text{CN})]^{2+}$, respectively. Also the spin–spin coupling ^{13}C –Tl to the two different thallium isotopes: ^{205}Tl : big peak, $I = 1/2$, 70.5%, and ^{203}Tl : small peak, $I = 1/2$, 29.5%, is seen in Fig. 1. In the ^1H NMR spectrum of the sample, two proton signals (2.80 and

Table 1
NMR data in aqueous solution ^a for [Ti(en)₂(CN)]²⁺ and for some related complexes

Compounds	²⁰⁵ Tl (δ, ppm)	¹³ C (δ, ppm)	¹ J(²⁰⁵ Tl– ¹³ C) (Hz)	¹ H (δ, ppm)
[Ti(CN)] ²⁺ [3]	2310	141.2	14 636	
[Ti(CN)] ²⁺ (this work)	2422	142.2	13 730	
[Ti(CN) ₂] ⁺ [3]	2414.4	142.0	13 749	
[Ti(CN) ₃] ⁺ [3]	2848.4	147.4	7954	
[Ti(en) ₂ (CN)] ²⁺ (this work)	2846	147.1; 39.71 (en)	7911	3.46 (–CH ₂ –)
[Ti(en)] ³⁺ [5]	2434	37.8		3.65 (–CH ₂ –)
[Ti(en) ₂] ³⁺ [5]	2659	37.5		3.47 (–CH ₂ –)
[Ti(en) ₃] ³⁺ [5]	2889	39.5		3.57 (–CH ₂ –)
[Ti(Tpp)(O ₂ CCF ₃)] [20a]	2662			
[Ti(Tpp)(CN)] [20a]	2839	135.9	5740	
en		41.68		2.80

^a Except for [Ti(en)]³⁺, [Ti(en)₂]³⁺ and [Ti(en)₃]³⁺ where the solvent was pyridine.

3.46 ppm) are present. By comparison with ¹H NMR and ¹³C spectra of the free ethylenediamine, these signals can be assigned: the signal at 2.80 ppm (41.7 ppm for ¹³C NMR) corresponds to the free en and the other one, at 3.46 ppm (39.7 ppm for ¹³C NMR) is the en coordinated to Ti(III). The coordination atoms of the Ti(III) complexes of [Ti(en)₂(CN)]²⁺ (C–Ti–N₄) and of [Ti(CN)]²⁺ (Ti–C) are different, so the carbon relaxation times of the coordinated cyanide of two complexes are not equal. In the previous study [5], it was found that en ligand exchange occurs in the complex [Ti(en)₂]³⁺. Hence, the ¹³C–Ti spin–spin coupling of [Ti(en)₂(CN)]²⁺ for the two isotopes (²⁰³Tl and ²⁰⁵Tl) is not resolved in the ¹³C NMR spectrum. With 25% Na¹³CN enrichment it is easy to discern the composition

Table 2
Selected crystal data for [Ti(en)₂(CN)](ClO₄)₂ (1) and [Ti(tren)(CN)₂](ClO₄) (2) ^a

	1	2
Empirical formula	C ₅ H ₁₆ Cl ₂ N ₅ O ₈ Ti	C ₈ H ₁₈ ClN ₆ O ₄ Ti
Formula weight	549.50	501.96
Temperature (K)	293(1)	293(1)
Crystal system	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	7.9697(12)	10.8940(10)
<i>b</i> (Å)	15.477(3)	11.9530(10)
<i>c</i> (Å)	5.9274(7)	11.8000(10)
<i>β</i> (°)		100.194(4)
<i>V</i> (Å ³)	731.1(2)	1512.4(3)
<i>Z</i>	2	4
<i>ρ</i> _{calc} (g cm ^{−3})	2.496(1)	2.126
<i>μ</i> (Mo Kα) (mm ^{−1})	11.457	10.88
<i>F</i> (000)	520	880
<i>N</i> (obs)	725	2820
Final <i>R</i> indices	<i>R</i> ₁ = 0.0390, <i>wR</i> ₂ = 0.1060	<i>R</i> ₁ = 0.0533, <i>wR</i> ₂ = 0.1160
[<i>I</i> > 2σ(<i>I</i>)]		
Largest difference peak and hole (e Å ^{−3})	5.637 and −1.706	1.057 and −1.571

^a *R* values are defined as: $R_{\text{int}} = \sum |F_o^2 - F_o^2(\text{mean})| / \sum [F_o^2]$,
 $S = [\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$, $R_1 = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$,
 $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$.

of two Ti(III) cyanide species using the spin–spin coupling (¹³C–²⁰⁵Tl) pattern observed in the ²⁰⁵Tl NMR spectrum of this sample (Figs. 1 and 2). In ²⁰⁵Tl NMR there are only two peaks, centered at 2422 and 2846 ppm, respectively, and two small peaks on both sides of these peaks. The same values of the spin–spin coupling constants for both species are obtained from both ¹³C and ²⁰⁵Tl NMR spectra. The middle peak of the three symmetric signals in ²⁰⁵Tl NMR originates from the non-enriched CN[−] coordinated thallium complex and the two small signals on the sides come from the enriched ¹³CN[−] coordinated thallium complexes. From the analysis of the peak integrals of ¹³C and ²⁰⁵Tl NMR spectra corresponding to the complexes [Ti(en)₂(CN)]²⁺ and [Ti(CN)]²⁺, based on total concentrations of Ti(III) and CN[−] in the solution, the ratios of Ti(III)/CN[−] in two complexes are 1:1; this ratio fits perfectly to the two ²⁰⁵Tl NMR spectra with the same pattern of spin–spin coupled signals. In this way the two species, [Ti(en)₂(CN)]²⁺ and [Ti(CN)]²⁺, can be unambiguously assigned in the solution (Table 1). From the data in Table 1, it can be seen that the chemical shift and the spin–spin coupling constant of the complex [Ti(en)₂(CN)]²⁺ are very similar to those of

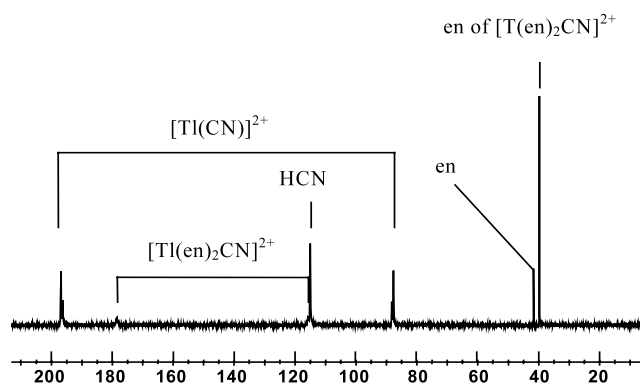


Fig. 1. Proton decoupled ¹³C NMR spectrum of an aqueous solution containing 50 mmol l^{−1} Ti(ClO₄)₃, 150 mmol l^{−1} NaCN and 60 mmol l^{−1} ethylenediamine. pH 2.5 (Na¹³CN was enriched in ¹³C to 25%).

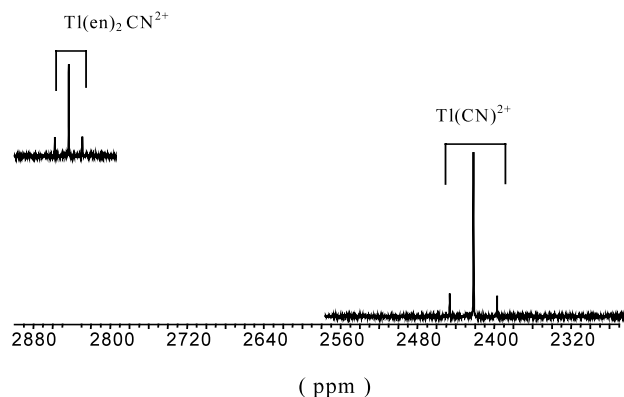


Fig. 2. ^{205}Tl NMR spectrum of the solution described in caption of Fig. 1.

the previously described complex $[\text{Tl}(\text{CN})_3]$ [4] (the complexes of $[\text{Tl}(\text{CN})_2]^+$, $[\text{Tl}(\text{CN})_3]$ and $[\text{Tl}(\text{CN})_4]^-$ do not exist in the presently studied solutions at this $\text{Tl(III)}/\text{CN}^-$ ratio, mainly due to the low pH value) [4]. The observed chemical shift of $[\text{Tl}(\text{CN})]^{2+}$ is somewhat different compared to the previous study (Table 1) [4]; it is mainly due to the effect of the ionic medium. Usually, the ^{205}Tl NMR chemical shift of not fully coordinated complexes is very sensitive to the medium [20a]. The ^{205}Tl NMR chemical shift of the complex $[\text{Tl}(\text{en})_2(\text{CN})]^{2+}$ is very close to that of the complex $[\text{Tl}(\text{tpp})(\text{CN})]$ (tpp: tetra-phenylporphyrin), because these two complexes have similar coordination environment with four nitrogen atoms and one carbon atom. ^{205}Tl NMR chemical shift increases with increasing coordination number both for the Tl(III) cyanide complexes and Tl(III) ethylenediamine complexes [4,5]. The ^{205}Tl NMR chemical shift of the complex $[\text{Tl}(\text{en})_2]^{3+}$ is 2659 ppm, hence shifted about 500 ppm to the high frequency compared to the solvated Tl(III) in pyridine [20a]. A similar chemical shift (2662 ppm) was observed for Tl(III) porphyrin complex, $[\text{Tl}(\text{tpp})(\text{O}_2\text{CCF}_3)]$; it shifted from 2662 to 2839 ppm when an extra cyanide was coordinated to form $[\text{Tl}(\text{tpp})(\text{CN})]$ [20a]. The chemical shifts of Tl(III) complexes with N-ligand shift to high frequency upon increasing en coordination to Tl(III) . It is compatible with the deshielding of the Tl nucleus when the electronegative nitrogen atoms coordinate to the Tl(III) leading to a decrease of the metal's d electron density. Earlier studies of cadmium complexes, also with d^{10} configuration similarly to Ti^{3+} , give an indication of the magnitude of this up-frequency change for different ligands, e.g. for N-donors [20b–e]. In the case of cyano complexes, an additional parameter is probably of importance, namely the back-donation of the electron density from the metal to the cyanide. The back-donation will cause lower shielding of the thallium nucleus and hence an increase in the metal NMR chemical shift. It is clear that cyanide coordination

causes an approximately 180 ppm increase in thallium NMR chemical shift for both $[\text{Tl}(\text{en})_2(\text{CN})]^{2+}$ and $[\text{Tl}(\text{tpp})(\text{CN})]$ complexes.

3.2. Crystal structures

3.2.1. $[\text{Tl}(\text{en})_2(\text{CN})](\text{ClO}_4)_2$ (**1**)

The structure was solved by single crystal X-ray diffraction technique. An ORTEP drawing of the cation is presented in Fig. 3(a). It is a linear supramolecule with cyanide bridging between two units of $[\text{Tl}(\text{en})_2]^{3+}$. The coordination geometry and the coordination number of Tl(III) is similar to $[\text{Tl}(\text{en})_3]^{3+}$ [5]. The difference is that

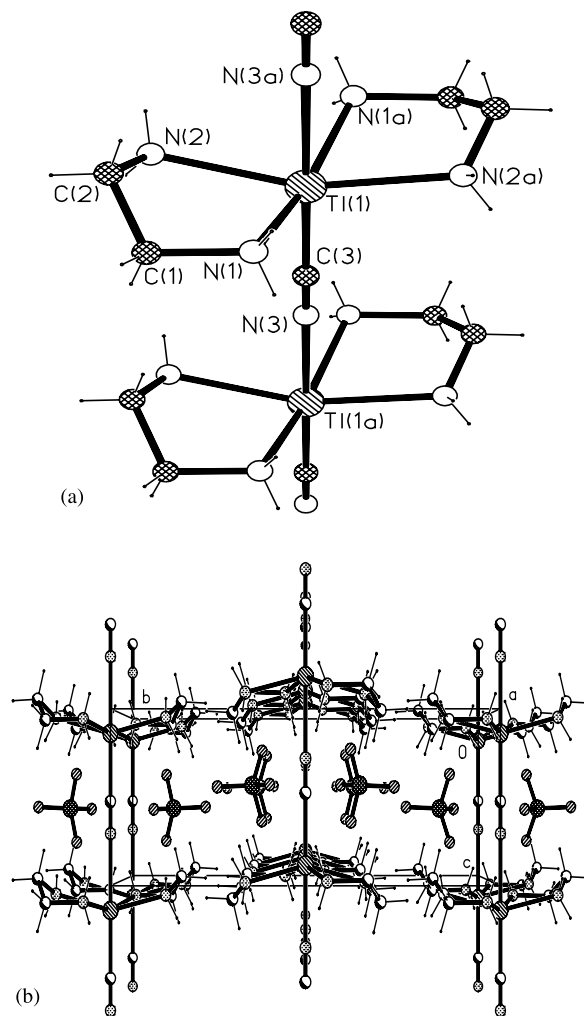


Fig. 3. (a) ORTEP perspective view of the cation in the crystal structure of $[\text{Tl}(\text{en})_2(\text{CN})]_n(\text{ClO}_4)_{2n}$ (thermal ellipsoids are drawn at 50% probability level). Relevant bond lengths (Å) and angles ($^\circ$): $\text{Tl}(1)-\text{C}(3)=2.28(2)$, $\text{Tl}(1)-\text{N}(1)=2.307(8)$, $\text{Tl}(1)-\text{N}(2)=2.311(9)$, $\text{Tl}(1)-\text{N}(3a)=2.571(17)$, $\text{N}(1)-\text{C}(1)=1.459(13)$, $\text{N}(2)-\text{C}(2)=1.420(16)$, $\text{N}(3)-\text{C}(3)=1.08(3)$, $\text{C}(1)-\text{C}(2)=1.547(17)$, $\text{N}(3a)-\text{Tl}(1)-\text{N}(1)=80.1(3)$, $\text{N}(1)-\text{Tl}(1)-\text{N}(1a)=160.2(7)$, $\text{N}(3a)-\text{Tl}(1)-\text{N}(2)=76.8(4)$, $\text{N}(1)-\text{Tl}(1)-\text{N}(2a)=98.1(3)$, $\text{N}(1)-\text{Tl}(1)-\text{N}(2)=77.3(3)$, $\text{N}(1)-\text{Tl}(1)-\text{C}(3)=99.9(3)$, $\text{N}(2)-\text{Tl}(1)-\text{C}(3)=103.2(4)$, $\text{N}(2)-\text{Tl}(1)-\text{N}(2a)=153.6(7)$. (b) A packing diagram for $[\text{Tl}(\text{en})_2(\text{CN})](\text{ClO}_4)_2$ viewed along the a axis.

the hexa-coordination of Tl(III) is made up of two cyanides, one through C and one through N, together with the four N of the en ligands. The bond distances of Tl(III)–N (–NH₂) (2.307–2.311 Å) are close to those in [Tl(en)₃]³⁺ (2.229–2.431 Å) [5] but much shorter than for Tl(III)–N (N≡C) (2.571 Å). The Tl–C (C≡N) bond distance in the title compound (2.28(2) Å) can be compared to the corresponding distances between Tl(III) and axial cyanide in porphyrin complexes [Tl(tpp)(CN)] (Tl(III)–C = 2.277(14) Å), [Tl(tmpp)(CN)] (Tl(III)–C = 2.218(5) Å) and [Tl(oep)(CN)] (2.220(4) Å) [21], and the edta complex Na₂[Tl(edta)(CN)]·3H₂O (2.14(3) Å) [13]. Hence, the presently determined distance is significantly longer than in most of the cited compounds, except for [Tl(tpp)(CN)]. The difference between these two complexes is that in the latter compound the Tl(III) center is situated about 0.908 Å above the porphyrin ring and cyanide is a terminal ligand, but in the title complex the metal is situated inside the square plane and the cyanide is a bridging bidentate ligand.

Interestingly, the parallel chains in the structure form one-dimensional channels in which the perchlorate ions are located (Fig. 3(b)). It could be expected that the perchlorates are disordered (with respect to more or less free rotation) as found in many crystal structures; however, the temperature factors do not give any support for this supposition. It is possible that replacing ClO₄[−] in this structure by a smaller anion would make a conducting material in which the anions could migrate along the channels.

It is important to mention that the structure of complex **1** is different in solution and in solid. In solution, Tl(III) is coordinated via four N atoms of en together with one cyanide through C atom. Normally, as in many previous studies e.g. [5, 20a], Tl(III) prefers hexa-coordination. The sixth coordinated atom is probably the O atom of a water molecule. In the solid the linear supramolecule forms, possibly due to the packing effects and the cyanide bridge.

3.2.2. [Tl(tren)(CN)₂](ClO₄) (**2**)

In this structure, the coordination around thallium is a distorted octahedron (Fig. 4), consisting of three nitrogen and one carbon atoms in the equatorial plane, and one nitrogen and one carbon in the apical positions. The two cyanides are in *cis* positions to each other, which is dictated by the tetradentate tren coordination. The C10–Tl1–C9 angle is 96.0°. The mean Tl–N and Tl–C bond lengths are 2.394(11) and 2.261(15) Å, respectively. The bond distances of Tl–N can be compared to the values 2.333–2.390 Å in [Tl(dien)₂]³⁺ [20f] and 2.229–2.431 Å in [Tl(en)₃]³⁺ [5].

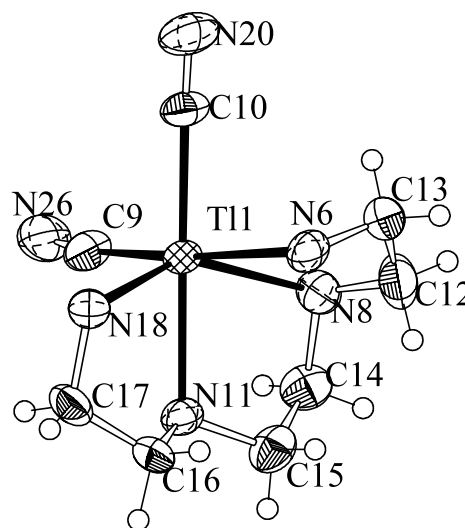


Fig. 4. ORTEP view of the cation structure in the crystal structure of [Tl(tren)(CN)₂](ClO₄) (thermal ellipsoids are drawn at 50% probability level). Relevant bond lengths (Å) and angles (°): Tl(1)–C(9) = 2.284(15), Tl(1)–C(10) = 2.233(13), Tl(1)–N(6) = 2.472(11), Tl(1)–N(8) = 2.399(10), Tl(1)–N(11) = 2.380(11), Tl(1)–N(18) = 2.333(12); C(10)–Tl(1)–C(9) = 96.0(5), C(10)–Tl(1)–N(11) = 174.7(5), C(10)–Tl(1)–N(18) = 101.9(5), N(18)–Tl(1)–N(11) = 74.4(4), C(10)–Tl(1)–N(8) = 106.7(5), N(6)–Tl(1)–N(8) = 73.0(4), N(20)–C(10)–Tl(1) = 177.6(15).

3.3. Raman spectrum of solid [Tl(en)₂(CN)](ClO₄)₂ (**1**)

In the Raman spectrum of the complex [Tl(en)₂(CN)]²⁺ in the solid, one strong vibration band at 2148 cm^{−1} was detected. It was assigned to the bridging cyanide ligand. The Raman vibration bands of cyanide terminally coordinated to Tl(III) were earlier detected in the range 2180–2200 cm^{−1} [3]. Comparing to the terminal cyanide, the bridging ligand shifts about 32 cm^{−1} to low frequency. Normally, in bridging cyano complexes $\nu(\text{C}\equiv\text{N})$ shifts to a higher frequency with σ -donation and shifts to a lower frequency with π -backbonding [22,23]. It was found for [Bu₄N]₂[Re₂(CN)(dppm)₂] that the four terminal cyanide ligands display stretches at 2097 and 2081 cm^{−1} and the two bridging cyanide ligands at 1935 cm^{−1} [24]. It indicates that the π -backbonding plays a major role in the (en)₂Tl–(CN)–Tl(en)₂ complex. Usually, $\nu(\text{M}–\text{N})$ symmetric stretching (391–485 cm^{−1}) and chelate deformation modes (291–404 cm^{−1}) of [M(en)₃]³⁺ and [M(en)₂]²⁺ ions are observed [22a]. The strong $\nu(\text{Tl}–\text{N})$ symmetric stretching and chelate deformation modes of [Tl(en)₂(CN)]²⁺ ion was detected at 437.4 and 320.6 cm^{−1}, respectively. One Tl–C vibration band at 460.3 cm^{−1} was considered to be the symmetric stretching vibration between thallium and carbon of the bridged cyanide. Similar M–C bands at 459 and 465 cm^{−1} were observed in [Au(CN)₄][−] and [Pt(CN)₄]^{2−} complexes, respectively [22b,22c].

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 149277 and 177376 for compounds **1** and **2**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@aacdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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