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Novel bis(diethylenetriamine)thallium(III) complex. Synthesis and characterization in pyridine solution and in solid

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Dedicated to Professor A.G. Sykes

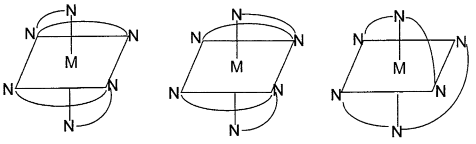
Abstract

A new complex of thallium(III) with the nitrogen donor ligand diethylenetriamine (dien) has been prepared and characterized by multinuclear NMR (^{1}H, ^{13}C, ^{205}Tl), infrared and Raman spectroscopy, and X-ray diffraction. In solution, the symmetric *s-facial* isomer of $[Tl(dien)_2]^{3+}$ is formed. This is a fluxional molecule even at low temperature (235 K); therefore, the different rotamers cannot be observed separately. A complete characterization of the complex is given from its non-trivial NMR spectra. The crystal structure of $[Tl(dien)_2](ClO_4)_3 \cdot H_2O$ shows *u-facial* geometry, where the coordination environment around thallium can be described as a distorted trigonal prism.

Keywords: Crystal structure; Thallium complexes; Polydentate amine complexes

1. Introduction

Coordination chemistry of thallium(III) has attracted considerable attention recently for its rich coordination geometry, though this metal ion is difficult to study in aqueous solution and in organic solvents due to its strong hydrolytic and oxidative properties [1,2]. Tl(III) is considered as a soft metal ion. Complexes with inorganic ligands, like chloride and bromide, have been studied previously [3–5]. Recently, the formation and equilibria of $[Tl(CN)_n]^{3-n}$ ($n = 1$–4) complexes have been studied by ^{205}Tl and ^{13}C NMR in aqueous solution and showed that Tl(III) forms very stable complexes with cyanide [6]. With *N*-donor ligands, like ethylenediamine, Tl(III) forms stable complexes with bidentate ligand coordination [7]. The coordination geometry of Tl^{3+}, due to its closed shell configuration, varies in different complexes, e.g. it is four-coordinated in $[Tl(CN)_4]^-$ and $[TlI_4]^-$ [5,8], five-coordinated in $TlBr_3(H_2O)_2$ [5], six-coordinated in $[Tl(H_2O)_6]^{3+}$, $[Tl(en)_3]^{3+}$ and $[TlCl_5(dmso)]^{2-}$ [7,9,10], seven-coordinated in $[Tl(edta)(OH)]^{2-}$, $[Tl(edta)(CN)]^{2-}$ and $[Tl(bipy)_3(dmso)]^{3+}$ [11–13] and eight-coordinated in $[Tl(bipy)_2(NO_3)_3]$, $[Tl(tpen)(NO_3)](ClO_4)_2$, $\{C(NH_2)_3\}_3 \cdot [Tl(nta)_2] \cdot 2H_2O$ and $Tl^I_3[Tl^{III}(nta)_2]$ [11,14]. (en = ethylenediammine, dmso = dimethylsulfoxide, edta = ethylenediaminetetraacetic acid, bipy = 2,2′-bipyridine, tpen = *N*,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)ethylenediamine, nta = nitrilotriacetic acid.)



Scheme 1. Conformers of $Tl(dien)_2$: (1) *s-facial*, (2) *u-facial*, (3) *mer*-isomer.

Diethylenetriamine, dien, is a tridentate ligand and its properties are similar to ethylenediamine. It is an extremely versatile organic ligand, especially in its complex steric conformations. Its coordination compounds

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with transition metal ions, such as Co(II), Cr(III), Cu(II) and Ni(II), have been investigated widely [15a,b]. For the bis(dien)Co(III) ion, the diethylenetriamine ligand coordination may exist in three geometrical isomers: *meridional*, *u-facial*, and *s-facial* (Scheme 1) and three structural conformations have been determined [15c–e]. The equilibrium distribution of the three geometric isomers depends on the environmental parameters, e.g. solvation, ion association, and temperature [15f].

So far no Tl–dien complexes have been described in the literature, the nitrate salt $[Tl(dien)_2](NO_3)_3$ has only been mentioned. It is soluble in water; under acidic conditions an immediate hydrolysis takes place, while in alkaline solution the decomposition of the complex takes about 24 h [11]. In order to investigate the rich coordination geometry of Tl(III) further, we report here the synthesis and characterization of Tl(III)–dien complexes in pyridine solution and in the crystal structure of $[Tl(III)(dien)_2](ClO_4)_3\cdot(H_2O)$.

2. Experimental

2.1. Preparation of stock solution

The chemical reagents were all of analytical grade. $TlClO_4$ was prepared by the reaction between Tl_2CO_3 (Aldrich, 99.95%) and an equivalent amount of $HClO_4$ and recrystallized from water. The stock solution of concentrated acidic $Tl(ClO_4)_3$ was prepared by anodic oxidation of $TlClO_4$. The concentrations of Tl(III) and perchloric acid were determined by titration with 0.1 M standard NaOH and $KBrO_3$ solutions after adding excess of solid NaCl to the analyzed solution, and using methyl orange as an indicator [16].

2.2. Preparation of solutions and NMR samples

The solutions were prepared by mixing different molar ratios of $Tl(CF_3CO_2)_3$ (Aldrich, analytical grade) and diethylenetriamine (Aldrich, analytical grade, 99%) in pyridine, or by mixing $Tl(ClO_4)_3$ and diethylenetriamine in aqueous solution. NMR samples containing the bis-complex in solution were prepared in two ways: (i) by dissolution of the $[Tl(dien)_2](ClO_4)_3\cdot H_2O$ crystal or (ii) by mixing solid $Tl(CF_3COO)_3$ (hydroscopic, contains small quantities of H_2O) and a dien solution in a suitable ratio. Both solutions were stable in time. Their ^1H NMR spectra are very similar, some differences appear only in the signal overlap in the NH region ($-NH_2$, –NH– groups) due to media effects. The corresponding ^{13}C NMR spectra are the same. All experiments were performed on both samples and the same results were obtained. In Section 3 the results for the sample in which $[Tl(dien)_2]^{3+}$ was prepared by mixing $Tl(CF_3COO)_3$ and dien in pyridine-d_5 are discussed.

2.3. Crystals of $[Tl(dien)_2](ClO_4)_3\cdot(H_2O)$

The crystals were obtained from 0.1 mol l^{-1} $[Tl(dien)_2]^{3+}$ perchlorate solution in water: 83 μl 1.2 mol l^{-1} acidic $Tl(ClO_4)_3$ in water (0.1 mmol) was slowly added to 1 ml aqueous solution of 0.3 mol l^{-1} diethylenetriamine under continuous stirring. A black precipitate was formed after the complete addition of the thallium perchlorate solution. After stirring for 30 min, the solid was dissolved forming a colorless solution. This final solution was stored in refrigerator, and after 2–3 days white rod-like crystals were obtained at the bottom of the flask.

2.4. NMR measurements

All samples were prepared in pyridine-d_5. NMR spectra were recorded in a Bruker DMX500 and AM400 spectrometers at various temperatures using a 5 mm inverse probehead and a 5 mm Tl probehead. The characteristic parameters: flip angle, pulse repetition time, spectral window, number of scans were chosen in order to obtain high-quality spectra and quantitative integration. The ^1H and ^{13}C NMR chemical shifts are reported in ppm from TMS; the positions of the pyridine signals were used for calibration. In ^{205}Tl NMR, the chemical shift values are referred toward higher frequencies from the signal of an infinitely diluted aqueous solution of $TlClO_4$. 1D and 2D spectra were recorded using standard Bruker pulse programs and the data were processed using Bruker WINNMR software. Spectra simulation was done using the Bruker NMRSIM program.

2.5. Raman and infrared spectra

Raman spectra of the crystalline compound **1** were obtained using a Renishaw System 1000 spectrometer equipped with a Leica DMLM microscope, a 25 mW diode laser (780 nm) and a Peltier-cooled CCD detector. Mid-infrared spectra were recorded by means of a Perkin–Elmer 1720 FT-IR spectrometer (a slice prepared by mixing the sample with dried KBr powder was used for measurement).

2.6. Crystal structure determination of $[Tl(dien)_2](ClO_4)_3\cdot(H_2O)\cdot$(**1**)

Suitable single crystals were selected and mounted on glass fibers with epoxy glue. Single-crystal X-ray diffraction data were collected on a Stoe image-plate diffractometer at $T = 110$ K. The unit cell dimensions are: $a = 18.571(2)$, $b = 8.1831(5)$, $c = 28.796(3)$ Å, $\beta = 94.274(10)°$ with $V = 4363.8(6)$ Å^3. Selected crystallographic data for **1** are presented in Table 1. Systematic absences in the collected diffraction data were consis-

Table 1
Crystal data and structure refinement parameters for compound $[Tl(dien)_2](ClO_4)_3{\cdot}(H_2O)$ (**1**)[a]

Empirical formula	$C_8H_{28}Cl_3O_{13}N_6Tl$
Formula weight	727.00
Temperature (K)	110(1)
Crystal system	monoclinic
Space group	$P2_1/a$ (no. 14)
Unit cell dimensions	
a (Å)	18.571(2)
b (Å)	8.1831(5)
c (Å)	28.796(3)
β (°)	94.274(10)
V (Å^3)	4363.8(6)
Z	8
Crystal size (mm)	0.07 × 0.10 × 0.25
ρ_{calc} (g cm^{-3})	2.210(1)
μ (Mo Kα) (mm^{-1})	7.84
Transmission factor range	0.342–0.400
$F(000)$	2832.0
N (collected), N (unique)	26 782, 8293
N_{obs}, N_{par}	4626, 548
R_{int} (all reflections)	0.173
S (Goodness-of-fit)	0.827
R_1, wR_2, $[I > 2\sigma(I)]$	0.0534, 0.0763
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.53 and −2.03

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

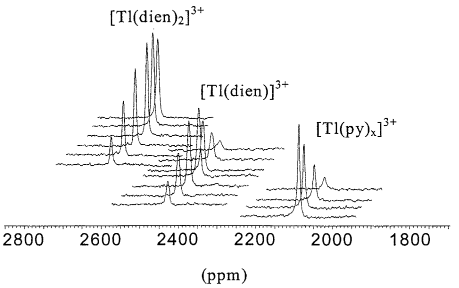


Fig. 1. ^{205}Tl NMR spectra of the thallium–dien system in pyridine solvent, no ionic medium. $[Tl(CF_3CO_2)_3] = 45$ mmol l^{-1}, [dien] = 0–200 mmol l^{-1}.

tent with space group $P2_1/a$ (no. 14). The data were corrected for absorption effects using the X-Shape program package [17]. The structure was solved using direct methods and refined against F^2 using the programs SHELXS97 and SHELXL97, respectively [18,19]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added at ideal positions and refined using a riding model.

3. Results and discussion

3.1. NMR characterization in solution

It is advantageous from NMR point of view if the central ion of the coordination compound studied is NMR active. Because of the 1/2 spin of Tl, the $[Tl(dien)_2]^{3+}$ complex can be studied by means of ^{205}Tl NMR (beside the usual ^{1}H and ^{13}C NMR). As will be shown below, in the present case only limited information could be obtained from ^{205}Tl NMR; moreover, the presence of the metal caused unexpected difficulties because of both scalar coupling and relaxation effects.

3.1.1. Tl NMR

It has been possible to trace the formed Tl–dien complexes in solution, since they are in slow chemical exchange range on the actual NMR time scale; hence, each of the complexes appeared as a separate signal in Tl NMR spectra. The position of the signal gives also an indication about the oxidation state of thallium in the complex, as the chemical shift regions for the different oxidation states are isolated from each other by about 2000 ppm [2]. Moreover, the Tl chemical shift is very sensitive to the sample parameters: temperature, concentration, anion type and solvent [20]. Keeping all this in mind, and using an NMR titration (Fig. 1), the ^{205}Tl NMR signals at 2450 and 2692 ppm were assigned to the complexes $[Tl(dien)]^{3+}$ and $[Tl(dien)_2]^{3+}$, respectively, which exist in equilibrium in solution. No other dien complexes are formed under the actual experimental conditions. At low dien/Tl ratios the solvated $[Tl(py)_x]^{3+}$ is formed; its chemical shift, 2085 ppm, is in agreement with recently reported results from this laboratory [7]. The chemical shifts of the complexes $[Tl(dien)_n]^{3+}$ ($n = 1-2$) shift to high frequency upon increasing n. It can be partially due to the deshielding caused by the coordination of the electronegative nitrogen atoms to Tl(III) which would lead to a decreasing d electron density on the metal ion. Several earlier studies of cadmium complexes, a d^{10} metal ion similar to Tl^{3+}, give an indication of the magnitude of this effect for different ligands (N-donors) [21–25]. The relationship between the chemical shifts and the number of coordinated dien ligands is linear (see Section 5); it shows that the effect of the first ligand on the electronic properties of Tl(III) is equal to that of the second one. This behavior is similar to that of the previously studied complexes $[Tl(en)_n]^{3+}$ ($n = 0-3$) [7]. A linear correlation between ^{113}Cd chemical shift and the number of coordinated ligands has also been observed for Cd–glycine complexes $[Cd(gly)_n]^{2-n}$ ($n = 0-3$) [26]. A theoretical calculation has been reported in Ref. [27] to explain the reason for such chemical shift change and this matter was discussed elsewhere [7].

However, these ^{205}Tl chemical shift data give only limited information about the solution structure; no other shift data in pyridine are available for comparison. Moreover, no coupling constant values could be resolved.

3.1.2. ^{13}C-NMR

The $^{13}C\{^{1}H\}$ NMR spectrum shows four signals with the same intensity, belonging to two doublets. The reason is Tl-coupling as it turned out from a measurement at a lower magnetic field (100 MHz for ^{13}C NMR), where the distance in Hertz between the signals of the doublets was the same as at 125 MHz.

3.1.3. ^{1}H-NMR

The ^{1}H NMR spectra consist of four peaks in the NH region (top 1D spectrum, Fig. 2, 5.4–6.0 ppm) and eight overlapping peaks in the $-CH_2-$ region (top 1D spectrum, Fig. 2, 2.5–3.7 ppm). The four peaks from the NH region form two doublets because of the ^{2}J(H,Tl) coupling. This was proved in the same way as for the ^{13}C spectrum, by measuring the sample at lower magnetic field (400 MHz for ^{1}H NMR). The 4:1 ratio of the doublets suggests a solution structure with symmetrical orientation, i.e. four equivalent $-NH_2$ groups and two equivalent $-NH-$ groups. This observation is also indicated by the simplicity of the ^{13}C spectrum. In order to support this structural information the eight peaks originating from the $-CH_2-$ protons have to be assigned. The striking property of these peaks is their large line width, ~30 Hz, while the signals of the pyridine solvent are only 1 Hz broad. The 1D spectrum does not contain enough information on peak assignment; therefore, 2D correlation spectra have been recorded. For clarity, the coupling scheme in the case of two non-equivalent H atoms of an isolated $-CH_2-$ group and Tl is shown in Scheme 2.

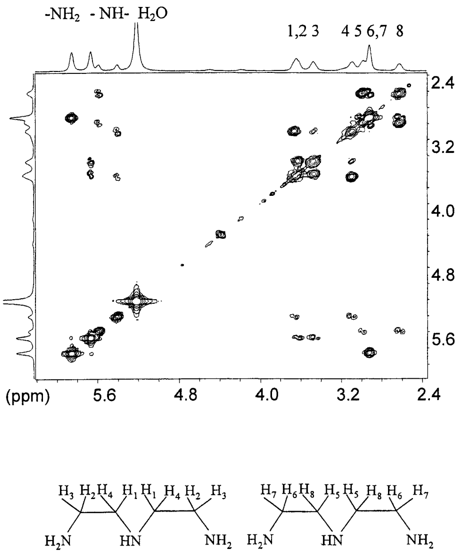
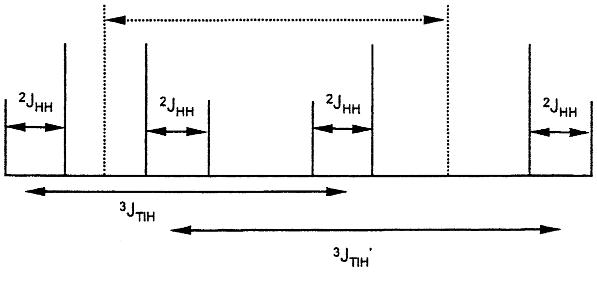


Fig. 2. $^{1}H-^{1}H$ COSY45 spectra of a sample containing $[Tl(dien)_2]^{3+}$ in pyridine-d_5. The inset shows the numbering scheme of the hydrogen atoms.



Scheme 2.

The scheme shows that each H, appearing as a doublet in the AB spin system, will couple with a different constant to Tl, in this case $^{3}J_{\mathrm{TlH}}$ and $^{3}J_{\mathrm{TlH'}}$. Usually, $^{2}J_{\mathrm{HH}}$ values are ~15 Hz. In the present case, the signals are broader and the fine structure is suppressed; hence, only one peak is observed. (In this context, it can be emphasized that the Tl coupling is *not* represented by the distance between the centers of the AB doublets shown in Scheme 2 by the dotted line.)

Furthermore, the coupled pairs of protons can be detected by the 2D HH COSY pulse sequence (Fig. 2). Cross-peaks with higher intensity show the *geminal* H–H protons of one $-CH_2-$ group, while the weaker cross-peaks come from the *vicinal* couplings between two neighboring $-CH_2-$ groups. For simplicity, the numbering 1–8 is introduced for ^{1}H signals in the $-CH_2-$ region (see Fig. 2). Two separate groups are detected, namely 1,2,3,4 (*geminal* coupling between 1–4 and 2–3 and *vicinal* coupling between 1–2 and 3–4); and 5,6,7,8 (*geminal* coupling between 5–8 and 6–7 (overlap) and *vicinal* coupling between 7–8 and 5–6 (overlap)). Weak cross-peaks between the neighboring $-CH_2-$ and $-NH-$ groups, as well as between $-CH_2-$ and $-NH_2$, are also detected. Thus, for one signal of the $-NH-$ group the 1–4, while for the other one the 5–8 $-CH_2-$ group is singled out. In a similar way, peaks 2–3 and 6–7 are assigned to the $-NH_2$ group.

To single out the H atoms belonging to the corresponding C nuclei 2D heteronuclear $^{1}H-^{13}C$ correlation spectrum was recorded (Fig. 3). Thus, protons 1–4 and 5–8 belong to the same carbon, and protons 2–3 and 6–7 belong to the other carbon atom.

In this way, all parts of the molecule have been assigned. The signals corresponding to the thallium spin Tl(α) are $H_2N-CH_2(2,3)-CH_2(1,4)-NH-CH_2(1,4)-CH_2(2,3)-NH_2$, while those corresponding to Tl(β) are $H_2N-CH_2(6,7)-CH_2(5,8)-NH-CH_2(5,8)-CH_2(6,7)-NH_2$. Bearing in mind that proton signals are broad and using Scheme 2 it can be deduced that the couplings $^{3}J_{\mathrm{TlH}}$ appear between signals 1–5, 4–8, and 2–6, 3–7, respectively. An overview of the NMR data obtained is shown in Table 2. To demonstrate the validity of these data the simulated spectrum has been calculated (Fig. 4). The simpler spectrum is obtained if besides the $^{3}J_{\mathrm{TlH}}$ values only the *geminal* $^{2}J_{\mathrm{HH}}$ coupling constants are included (Fig. 4(a)). In reality, *vicinal*

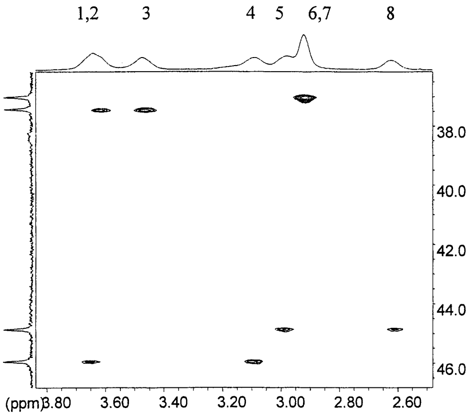


Fig. 3. $^1H-^{13}C$ 2D correlation spectra via double INEPT with inverse detection and gradient pulses, of a sample containing $[Tl(dien)_2]^{3+}$ in pyridine-d_5.

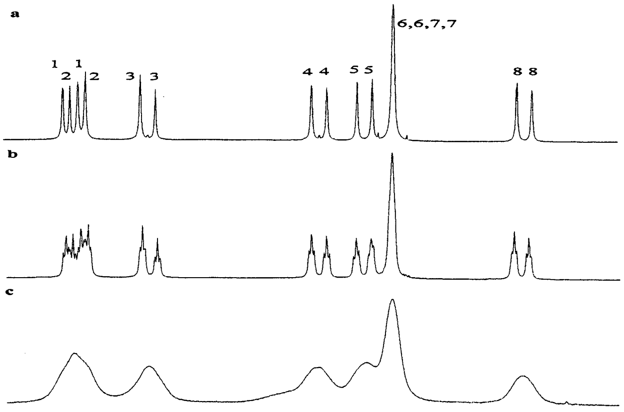


Fig. 4. Simulated (a, b) and experimental (c) ^1H NMR spectra of $[Tl(dien)_2]^{3+}$ in pyridine, $-CH_2-$ region. (a) Only $^3J_{TlH}$ and $^2J_{HH}$ couplings are considered, and (b) also $^3J_{HH}$ couplings are included. The numbers are provided for an easier identification of the signals.

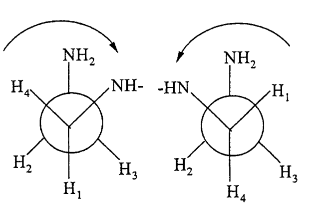
$^3J_{HH}$ couplings are also present leading to a more complicated spectrum (Fig. 4(b)). It is clear that an intramolecular motion causes the overlap of these signals, but the characterization of this motion is outside the scope of this structural study. Nevertheless, using a ball-and-stick model of the molecule it can be observed that there are two limiting rotamer conformations between which a fluxional motion can exist (cf. Scheme 3).

In an attempt to visualize these rotamers a temperature study down to 235 K was performed, but the signals of ^1H NMR did not split and did not become narrower.

In conclusion, it can be stated that under the current circumstances, in pyridine solution, only the *s-facial* structural isomer of $[Tl(dien)_2]^{3+}$ is formed. The NMR techniques used made it possible to extract structural information from the non-trivial spectra of this fluxional molecule.

3.2. Raman and infrared spectra in solid

Assignment of the bands in the vibrational spectra is based on the comparison with the data for the free



Scheme 3.

dien ligand and literature data for some related metal ion–dien complexes [28]. In the IR spectrum, the complex $[Tl(dien)_2](ClO_4)_3$ shows three bands in the region 3000–3250 cm^{-1} (at 3091, 3137 and 3221 cm^{-1}) which are assigned to $-NH_2$ and –NH– stretching motion, in a similar way as for [Pd(dien)X]X [28]. The $-NH_2$ bending is observed in the region 1500–1600 cm^{-1}: the bands at 1571 and 1439 cm^{-1} are due to the $-NH_2$ and –NH– groups, respectively. The metal–nitrogen stretching vibrations appear at 560 and 509 cm^{-1}. The Raman spectrum of $[Tl(dien)_2](ClO_4)_3$ complex shows N–H vibration bands of the coordinated dien at 2976, 2961 and 2903 cm^{-1} and Tl–N vibration bands at 420

Table 2
NMR data of a solution containing $[Tl(dien)_2]^{3+}$ in pyridine

Nucleus	δ (ppm)	LW (Hz)	^nJ(Tl,H) (Hz)	^2J(Tl,C) (Hz)	^1J(C,H) (Hz)	Assignment
^1H	3.314	~30	$^3J = 330$			$-CH_2-NH-$
	2.857	~30	$^3J = 230$			$-CH_2-NH-$
	3.284	~30	$^3J = 361$			$-CH_2-NH_2$
	3.199	~30	$^3J = 275$			$-CH_2-NH_2$
	5.31	~25	$^2J = 94$			–NH–
	5.76	~25	$^2J = 92$			$-NH_2$
^{13}C	37.3	6		51	141; 143	$-CH_2-NH_2$
	45.4	6		137	144; 136	$-CH_2-NH-$
^{205}Tl	2692	~1000				

and 294 cm^{-1}, as usual [29]. All the frequencies observed in the vibrational spectra and the assignment proposed for compound **1** are listed in Table 3.

Table 3
Observed frequencies in vibrational spectra and proposed assignment for the solid compound $[Tl(dien)_2](ClO_4)_3 \cdot (H_2O)$ (**1**)

Raman ν (cm^{-1})	IR ν (cm^{-1})	Assignment
	3221, 3137, 3091	$\nu(NH_2$ or $NH)$
2961, 2903	2961,2928,2889,2861	$\nu(CH_2)$
1583	1571	$\delta(NH_2)$
1476	1456	$\delta(CH_2)$
	1439	$\delta(NH)$
1393	1317	$w(CH_2)$
1363		$t(CH_2)$
1320, 1142		$w(NH_2)$
1271, 1231	1143	$t(NH_2)$
1094	1113, 1088	$\nu_3(ClO_4^-)$
1071, 1041, 1012, 974	1041, 1007	$\nu(CC)$, $\nu(CN)$
	995	$t(NH_2)$
933	940	$\nu_1(ClO_4^-)$
867		$\rho(CH_2)$
816		$\nu(CN)$
	748, 669	$\rho(NH_2)$
625	636, 626	$\nu_4(ClO_4^-)$
447		$\nu_2(ClO_4^-)$
420, 294	560, 509	$\nu(Tl–N)$
512		$\delta(NCCN)$
277	419	$\delta(NCC)$
345		$\tau(NH_2)$
257, 215		$\delta(N–Tl–N)$
181		$\tau(NCCN)$

Table 4
Selected bond lengths (Å) and bond angles (°) for compound $[Tl(dien)_2](ClO_4)_3 \cdot (H_2O)$ (**1**)

Bond lengths			
Tl1–N1	2.372(8)	Tl2–N7	2.390(8)
Tl1–N2	2.385(6)	Tl2–N8	2.371(6)
Tl1–N3	2.370(8)	Tl2–N9	2.360(8)
Tl1–N4	2.387(8)	Tl2–N10	2.333(9)
Tl1–N5	2.353(7)	Tl2–N11	2.386(6)
Tl1–N6	2.356(7)	Tl2–N12	2.345(8)
Bond angles			
N1–Tl1–N2	75.6(3)	N8–Tl2–N7	76.8(2)
N1–Tl1–N4	82.9(3)	N8–Tl2–N11	129.4(2)
N2–Tl1–N4	143.9(2)	N9–Tl2–N7	121.2(3)
N3–Tl1–N1	118.2(3)	N9–Tl2–N8	75.0(3)
N3–Tl1–N2	75.6(3)	N9–Tl2–N11	86.4(3)
N3–Tl1–N4	90.1(3)	N10–Tl2–N7	89.5(3)
N5–Tl1–N1	146.5(3)	N10–Tl2–N8	87.5(3)
N5–Tl1–N2	134.9(3)	N10–Tl2–N9	138.6(3)
N5–Tl1–N3	87.7(3)	N10–Tl2–N11	76.2(3)
N5–Tl1–N4	75.8(3)	N10–Tl2–N12	117.6(3)
N5–Tl1–N6	76.1(3)	N11–Tl2–N7	148.3(3)
N6–Tl1–N1	91.6(3)	N12–Tl2–N7	85.7(3)
N6–Tl1–N2	92.3(2)	N12–Tl2–N8	149.4(3)
N6–Tl1–N3	142.6(3)	N12–Tl2–N9	93.6(3)
N6–Tl1–N4	117.2(3)	N12–Tl2–N11	76.7(3)

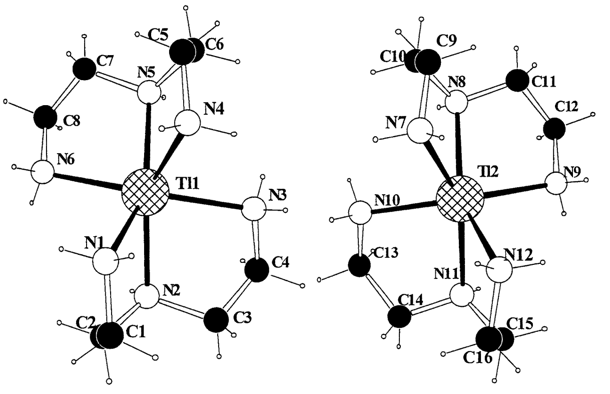


Fig. 5. The two, structurally different, conformations of $[Tl(dien)_2]^{3+}$ found in the solid state.

3.3. Solid state structure of $[Tl(dien)_2](ClO_4)_3 \cdot (H_2O)$ (1)

Compound **1** crystallizes in the monoclinic space group $P2_1/a$ with eight formula units per unit cell. The asymmetric unit contains two crystallographically independent $[Tl(dien)_2]$ entities with distinct conformations and an uncoordinated water molecule. Selected bond lengths and angles for the two Tl distinctive cations are given in Table 4. In both complexes, the central Tl atom is bonded to six dien N atoms. The structure of the two isomers is shown in Fig. 5. The coordination environment around the Tl atom can be described as a distorted trigonal prism in both cations although the geometries of the two complexes differ slightly. An analysis of the closest coordination environment of both cations (using the computer programs PLATON and SYMMOL [30]) indicate that both complexes are non-symmetric. In the Tl1 complex the Tl–N bonds are in the range 2.353(7)–2.387(8) Å, while in the Tl2 complex the Tl–N bonds are in the range 2.333(9)–2.390(8) Å. The Tl–N bond distances fall in the same range as those in $[Tl(en)_3]^{3+}$, 2.229(13)–2.431(14) Å [7]. In $[Tl(edta)(CN)]^{2-}$ the distances are somewhat longer, 2.41(2)–2.43(2) Å [12], which is due to the higher thallium coordination number (seven) in the latter compound. For the closed shell d^{10} Tl(III) ion, the coordination geometry is usually dependent on the properties of the donor atoms of the ligands. For iodide and cyanide, tetrahedral $[TlI_4]^-$ and $[Tl(CN)_4]^-$ are formed [5,8]. For ligands coordinating via nitrogen, coordination number six is the most common and has been found in the two recent crystal structures containing $[Tl(dien)_2]^{3+}$ (herein) and $[Tl(en)_3]^{3+}$ [7].

In the previously studied *u-facial*-bis(diethylenetriamine)cobalt(III) complex [15d], the diethylenetriamine ligand coordination is as in Scheme 1; the *u-facial* isomer was found to exist in two forms differing only in the orientation of the carbon atoms in the chelate ring system. In the present study, in the crystal structure of **1** containing the $[Tl(dien)_2]^{3+}$ cation, a *u-facial* isomer appears in two isomers related by nearly a mirror plane. This structure is similar but has a slightly bigger distortion compared with the cobalt species, which is probably due to the larger ionic radius of Tl(III) compared with Co(III) (Tl^{3+}: 0.95 Å (CN = 6) and Co^{3+}: 0.69 Å (low spin), 0.75 Å (high spin) (CN = 6)) [31].

4. Conclusion

Tl(III)–dien complexes have been synthesized and characterized both in solution and solid. In solution, two stereochemically different carbon atoms are present in $[Tl(dien)_2]^{3+}$, thus, an *s-facial* isomer is formed. Intramolecular motion within the coordinated ligand chains is present even at low temperature (235 K) but the conformations could not be distinguished by ^{13}C and ^{1}H NMR spectroscopy.

In the crystal structure of $[Tl(dien)_2](ClO_4)_3 \cdot H_2O$, there are two isomeric *u-facial* $[Tl(dien)_2]^{3+}$ entities in the asymmetric unit related to each other by nearly a mirror plane.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 160270 for the two isomers $[Tl(dien)_2](ClO_4)_3$. 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@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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