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A novel bonding mode of tetrazolate ligand to a metal: synthesis and structural characterization of 5-phenyltetrazolate organolanthanide complexes: $[\{(C_5H_4Me)(C_5H_5)LnTz\}_2][\{(C_5H_4Me)_2LnTz\}_2]$ (Ln = Dy, Gd) and $[(C_5H_4Me)_2LnTz)]_2$ (Ln = Yb, Er)

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Abstract

Reaction of $(C_5H_4Me)_3Ln$ and TzH (5-phenyl-1H-tetrazole) in THF affords complexes $[(C_5H_4Me)_2LnTz]_2$ [Ln = Yb (**1**), Er (**2**)]. **1** crystallized in the space group $C2/c$, with unit cell dimensions $a = 25.596(2)$, $b = 8.342(1)$, $c = 21.573(2)$ Å, $\beta = 129.322(9)°$. $V = 3563.5(8)$ Å^3 and $Z = 8$ for $D_c = 1.776$ g cm^{-3}. Least-squares refinement of the model based on 2700 reflections converged to a final $R = 0.031$. The molecule is centrosymmetric dimer in which each ytterbium atom is coordinated by two methylcyclopentadienyl groups and three nitrogen atoms of the bridging Tz ligands to form a distorted trigonal-bipyramidal geometry. When there is a small amount of $(C_5H_4Me)_2Ln(C_5H_5)$ in $(C_5H_4Me)_3Ln$, the 1:1 complexes $[\{(C_5H_4Me)(C_5H_5)LnTz\}_2][\{(C_5H_4Me)_2LnTz\}_2]$ (Ln = Dy (**3**), Gd (**4**)) were obtained in crystalline form. **3** and **4** crystallize as isomorphous crystals of space group $P\bar{1}$ with the following unit cell parameters (**3**/**4**): $a = 9.374(2)/9.420(4)$, $b = 13.048(2)/13.215(4)$, $c = 16.542(4)/16.677(5)$ Å, $a = 86.95(2)/87.24(2)$, $\beta = 74.61(1)/74.50(3)$, $\gamma = 77.31(1)/77.08(3)°$, $Y = 1903(1)/1950(1)$ Å^3, $Z = 2$, $D_c = 1.602/1.545$ g cm^{-3}, $R = 0.046/0.051$. Crystallographic data for **3** and **4** show that there are two disconnected structural units $[(C_5H_4Me)(C_5H_5)Ln(\mu\text{-}\eta^1{:}\eta^2\text{-Tz})]_2$ and $[(C_5H_4Me)_2Ln(\mu\text{-}\eta^1{:}\eta^2\text{-Tz})]_2$, crystallizing in one asymmetrical unit, each of which is tetrazolate-bridged dimer and has an inversion center. The bridging unit Ln_2N_6 is planar. All three structures reveal an unusual bonding mode of the tetrazolate ligand, in which the tetrazolate group acts as both a bridging and chelating ligand, with the nitrogen atoms at 1, 2 and 3-position taking part in bonding. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ytterbium; Erbium; Dysprosium; Gadolinium; Organolanthanide; Structure; Tetrazolate; Methylcyclopentadienyl

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1. Introduction

The chemistry of organolanthanides has experienced extremely important developments during the last two decades, and numerous unusual compounds with unprecedented structures and reactivity patterns have been prepared. It was realized that the large size of the lanthanide elements, their high electropositivity and oxophilicity could lead to a unique organometallic chemistry [1–4]. However, most of the chemistry so far has been based on the cyclopentadienyl-, modified cyclopentadienyl-, and cyclooctatetraenyl-type ligands. It is attracting growing attention how to find some alternatives to cyclopentadienyl, which can be used for synthesizing new organolanthanide complexes with novel structures, physical properties and reactivities [5–8].

Tetrazole bears a formal resemblance to cyclopentadiene. As a ligand, it possesses an interesting coordina-

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tion chemistry [9–12]. Each of the four nitrogen atoms of the tetrazole ring, in principle, is capable of acting a coordination site. The nucleophilicity of the nitrogen and their steric accessibility may be varied through appropriate ring substitution. Variable modes of coordination for these ligands have been found. For example, the tetrazolate anions can coordinate to metals as monodentate, exo-bidentate, 1,2,4-tridentate, or a delocalized η^5–π system. Despite these attractive features, the development of tetrazole coordination chemistry is primarily focused on the main- and transition-metals, and their organolanthanide chemistry, until now, has been limited [13]. In order to continue our recent investigations of N-containing systems [4,14], and to provide further information concerning the details of bonding to the metal ions of coordinated tetrazolates, in this paper, we report first the synthesis and the X-ray crystal structure of tetrazolate organolanthanide complexes with methylcyclopentadienyl or cyclopentadienyl co-ligands. This study represents a novel mode of bonding of tetrazolate to metal ions.

2. Results and discussion

2.1. Syntheses and spectroscopic characterization of *1–4*

The reaction of $(C_5H_4Me)_3Ln$ with equimolar amount of 5-phenyl-1H-tetrazole (HTz) results in the isolation in good yields of complexes $[(C_5H_4Me)_2LnTz]_2$ [Ln = Yb (**1**), Er (**2**)]. However, attempts to synthesize complex $[(C_5H_4Me)_2PrTz]_2$ by the similar reaction were unsuccessful due to the markedly stable complex $Pr(Tz)_3$. On the other hand, in the course of preparing $[(C_5H_5Me)_2DyTz]_2$ and $[(C_5H_4Me)_2GdTz]_2$, we have obtained single crystals of 1:1 complexes $[\{(C_5H_4Me)(C_5H_5)DyTz\}_2][\{(C_5H_4Me)_2DyTz\}_2]$ (**3**) and $[\{(C_5H_4Me)(C_5H_5)GdTz\}_2][\{(C_5H_4Me)_2DyTz\}_2]$ (**4**), which preferentially crystallized from a reaction containing an apparent mixture of $(C_5H_4Me)_3Ln$ and $(C_5H_4Me)_2Ln(C_5H_5)$. Presumably there may be a small amount of cyclopentadiene in methylcyclopentadiene, resulting in the presence of $(C_5H_4Me)_2Ln(C_5H_5)$ in $(C_5H_5Me)_3Ln$ (Ln = Dy, Gd). Due to the acidity of cyclopentadiene is stronger than that of methylcyclopentadiene and the proton-exchange reaction of TzH and methylcyclopentadienyl anion takes place more readily than that of TzH and cyclopentadienyl anion does, thus the reaction of $(C_5H_4Me)_2Ln(C_5H_5)$ and TzH yielded mainly complex $[(C_5H_4Me)(C_5H_5)LnTz]_2$ other than $[(C_5H_4Me)_2LnTz]_2$. Attempts to obtain pure $[(C_5H_4Me)(C_5H_5)LnTz]_2$ directly from the reaction of $(C_5H_4Me)_2Ln(C_5H_5)$ and TzH are undergoing. The title complexes are soluble in THF and $C_6H_5CH_3$ but less soluble in *n*-hexane. They are highly sensitive toward air and water.

The IR spectra of complexes **1**–**4** show characteristic absorptions of $\nu_{C=N}$ and $\nu_{N=N}$ for the free 5-phenyl-1H-tetrazole at 1484 and 1409 cm^{-1} [15,16] are shifted on complexation to lower frequencies at ca. 1446 and 1350 cm^{-1}, respectively. These shifts are analogous to those previously reported for cyclopentadienyl complexes [17], and could result from delocalization of the negative charge into the ring of the tetrazolate anion, which gives the ring a partial aromatic characterization. The molecular ions and main fragments of all the four complexes are clearly observed in the mass spectra, indicating that the binuclear core is present. Significantly, the data show that the 5-phenyltetrazolate group of the resulting ions is less stable, and breaks easily under electron impact, thereby being more easily lost as fragment of PhCN first. This conforms to the facts that the nitrogen atoms involved in the coordination on the Tz ring are at 1, 2 and 3 positions in dimeric molecule and that the part of non-bonded to metal for the Tz ligand is extruded more easily than that of bonded to metal.

It is interesting to note that when the evaporation temperature of the samples reaches a certain value for each, not only is the molecular ion peak $[\{(C_5H_4Me)_2LnTz\}_2]^{\cdot+}$ or $[\{(C_5H_4Me)(C_5H_5)LnTz\}_2]^{\cdot+}$ observed in the spectra, but also the peaks corresponding to $(C_5H_4Me)_3Ln^{\cdot+}$, $(C_5H_4Me)_2Ln(C_5H_5)^{\cdot+}$ or $(C_5H_4Me)Ln(C_5H_5)_2^{\cdot+}$ as well as their fragments are observed as well [18]. At the same time, for compounds **2**–**4** the peaks corresponding to $LnTz_3^{\cdot+}$ ions also appear. Furthermore, with the increase of evaporation temperature, the molecular ion peaks gradually disappear and the peaks of $Cp_3Ln^{\cdot+}$ enhance. In view of our previous studies [19,20], we deduce that compounds **1**–**4** may be unstable to heat and the following disproportionation reactions may take place under high temperature:

$$3[(C_5H_4Me)_2LnTz]_2 \rightarrow 2(C_5H_4Me)_3Ln + LnTz_3 \quad Ln = Yb, Er, Dy, Gd \qquad (1)$$

$$3[(C_5H_4Me)(C_5H_5)LnTz]_2 \rightarrow 2(C_5H_4Me)_2Ln(C_5H_5) + 2(C_5H_5)_2Ln(C_5H_4Me) + 2Ln(Tz)_3 \quad Ln = Dy, Gd \qquad (2)$$

The experimental results indicate that the disproportionation temperature of $[(C_5H_4Me)_2LnTz]_2$ and $[(C_5H_4Me)(C_5H_5)LnTz]_2$ tend to rise with decrease of the radii of Ln^{3+}, In fact $(C_5H_4Me)_2PrTz$ in THF decomposes to give $(C_5H_4Me)_3Pr$ and $PrTz_3$ at room temperature. The reason for the change of thermal stability of $[(C_5H_4Me)_2LnTz]_2$ with the lanthanide contraction, is presumably a result of the coordination unsaturation. The complexes of the lighter lanthanides, which have larger ionic radii, are more coordination unsaturated and their intermolecular redistributions take place more readily.

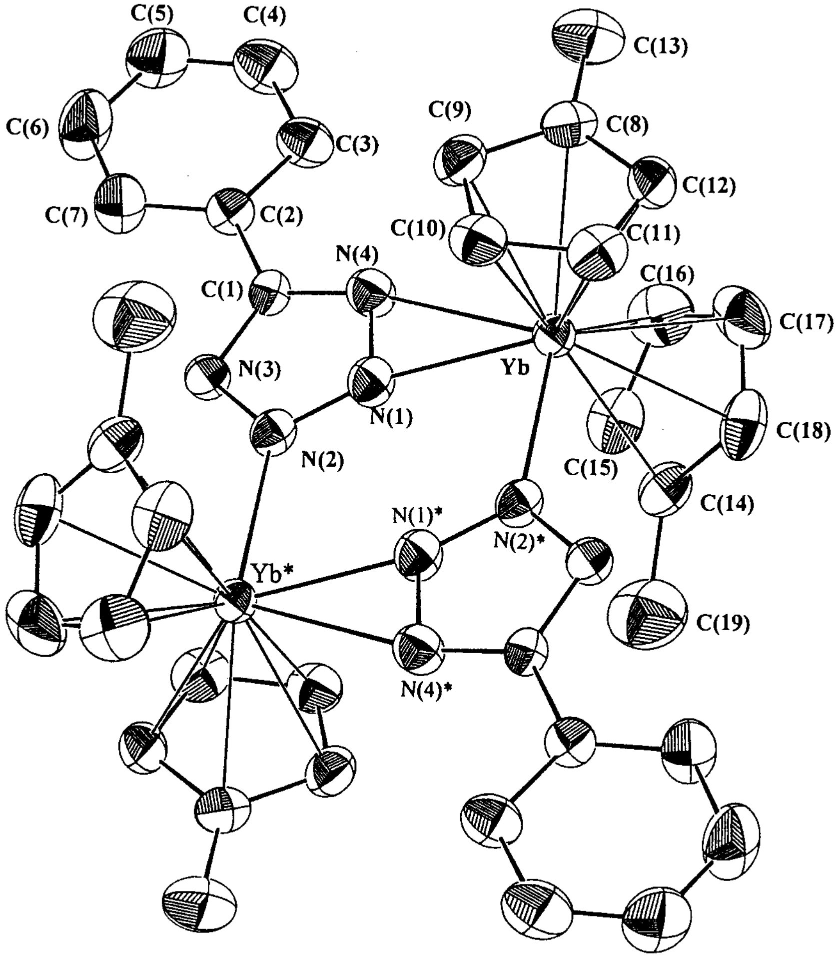


Fig. 1. Molecular structure of $[(C_5H_4Me)_2Yb(\mu\text{-}\eta^1\text{:}\eta^2\text{-Tz})]_2$.

2.2. Crystal structure of $[(C_5H_4Me)_2Yb(\mu\text{-}\eta^1\text{:}\eta^2\text{-Tz})]_2$ (1)

As shown in Fig. 1, the structure of **1** consists of discrete dimeric units with the two molecules hold together by bridging 5-phenyltetrazolate groups (Table 1). The bridging 5-phenyltetrazolates are tridentate and coordinate to the ytterbium atoms through three nitrogen atoms at the 1-, 2- and 3-positions. Two tetrazolate rings and two ytterbium atoms are planar. This reveals an unusual bonding mode of the tetrazolate ligand, in which the tetrazolate group acts as both a bridging and chelating ligand.

The ytterbium ion is coordinated by two η^5-C_5H_4Me groups and three N atoms of the 5-phenyltetrazolate ligands leading to a edge-bridged tetrahedral geometry [21]. The coordination number of ytterbium atom is nine and is not as common as eight for trivalent Cp_2Yb systems. The average Yb–C (ring) distance of 2.578(7) Å is at the low end of the range typical for trivalent dimeric organoytterbium complexes, and is in good agreement with the value found in $(C_5H_4Me)_3Yb_4(\mu\text{-}Cl)_6(\mu_3\text{-}Cl)(\mu_4\text{-}O)(THF)_3$ [2.59(2) Å] [22]. This result may be understood by a decrease in the intraligand repulsion since the exo-bidentate coordination of the tetrazolate bridge makes $(C_5H_4CH_3)_2Yb$ units far from each other. Consistent with this, the cent–Yb–cent angle of 129.3° is larger than those found in the more steric crowded compounds: $[(C_5H_5)_2Gd(ONCMe_2)]_2$, 126.3° [14]; $[(C_5H_4Me)_2Yb(THF)]_2O$, 124.8° [23], and is similar to that found in $[(C_5H_5)_2Y(OH)]_2(C_2Ph_2)$, 130.1° [24].

There are two distinctive metal–nitrogen distances in complex **1**. The Yb–N(1) and Yb–N(2)* distances of 2.325(5) and 2.383(5) Å are between those expected for an Yb^{3+}–N single bond and an $Yb^{3+} \leftarrow$:N donor bond [25–27], while the Yb–N(4) length of 2.690(5) Å is in the range of observed $Ln^{3+} \leftarrow$:NR_3 [13]. It is noteworthy that the Yb–N (donating) distance is one of the longest observed in organolanthanide structures, and is much longer than the values reported for a simple Yb←:N donating bond in $(C_5Me_5)_2Yb(TePh)(NH_3)$, 2.50(1) Å [26], and $[(C_5H_5)_3Yb]_2(\mu\text{-}NC_4H_4N)$, 2.61 Å [27]. The rather long distance between the Yb^{3+} and N(4) may be attributed to both the rigidity of the tetrazolate ring and the steric crowding from the bulky phenyl group.

2.3. Structure of $[(C_5H_4Me)(C_5H_5)Dy(\mu\text{-}\eta^1{:}\eta^2\text{-}Tz)\}2][\{(C_5H_4Me)_2Dy(\mu\text{-}\eta^1{:}\eta^2\text{-}Tz)\}_2]$ (**3**)

Structural analysis shows that the crystal of **3** (Table 2) consists of two complexes $[(C_5H_4Me)_2Dy(\mu\text{-}\eta^1{:}\eta^2\text{-}Tz)]_2$ (**3a**) and $[(C_5H_4Me)(C_5H_5)Dy(\mu\text{-}\eta^1{:}\eta^2\text{-}Tz)]_2$ (**3b**). From Fig. 2 it can be seen that both $[(C_5H_4Me)(C_5H_5)Dy(\mu\text{-}\eta^1{:}\eta^2\text{-}Tz)]_2$ and $[(C_5H_4Me)_2Dy(\mu\text{-}\eta^1{:}\eta^2\text{-}Tz)]_2$ are tetrazolate-bridged dimers and have an inversion center. In complex **3a** two methylcyclopentadienyl groups and three nitrogen atoms of 5-phenyltetrazolate ligands are coordinated to Dy^{3+} with the coordination number of nine. The geometry of **3a** is a edge-bridged tetrahedral and is nearly identical to that of complex **1**.

In **3a** the Dy(1)–N bond lengths of 2.360(6), 2.470(6) and 2.563(7) Å are not equal, which is consistent with that observed in **1**. The Dy(1)–N(2) and Dy(1)–N(3)* lengths are between the values typical for a Ln–N single bond and a N:→Ln donor one [27] and are consistent with the corresponding values found in $[(C_5H_4Me)Dy(\eta^2\text{-}PzMe_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}OSiMe_2PzMe_2)]_2$, 2.344(5) and 2.454(5) Å [28], respectively. The Dy(1)–N(1) length is in the range of observed Ln^{3+} ←:N donating bond [29]. If the difference between Dy^{3+} and Yb^{3+} radii is considered [30], the Dy(1)–N(2) distance of 2.360(6) A is comparable to that in **1**, 2.325(5) Å but the Dy(1)–N(3)* distance of 2.470(6) Å is greater than the corresponding value in **1**, 2.383(5) Å, and the distance of Dy(1)–N(1) [2.563(7) Å] is somewhat smaller than that observed in **1**, 2.690(5) Å. This shows that the donating coordination of Ln^{3+} and N atom at 1-position of 5-phenyltetrazolate should be enhanced with Ln^{3+} radii increasing.

Table 1
Selected bond distances (Å) and angles (°) of complex **1**

Yb–C(8)	2.572(7)	Yb–C(9)	2.584(7)
Yb–C(10)	2.580(6)	Yb–C(11)	2.575(7)
Yb–C(12)	2.567(7)	Yb–C(14)	2.611(6)
Yb–C(15)	2.604(7)	Yb–C(16)	2.569(8)
Yb–C(17)	2.558(7)	Yb–C(18)	2.562(7)
Yb–Cent1[a]	2.290	Yb–Cent2	2.288
Yb–N(1)	2.325(5)	Yb–N(2)*	2.383(5)
Yb–N(4)	2.690(5)	N(1)–N(2)	1.307(7)
N(1)–N(4)	1.342(7)	N(2)–N(3)	1.340(6)
N(3)–C(1)	1.340(6)	N(4)–C(1)	1.337(7)
		C(1)–C(2)	1.475(8)
N(1)–Yb–N(2)*	79.3(2)	N(1)–Yb–N(4)	29.9(2)
N(2)*–Yb–N(4)	109.3(2)	N(1)–N(2)–Yb*	120.8(4)
N(2)–N(1)–Yb	159.5(4)	N(4)–C(1)–C(2)	125.1(5)
N(4)–C(1)–N(3)	111.4(5)	N(3)–C(1)–C(2)	123.5(5)
N(2)–N(1)–N(4)	109.9(4)	Cent1–Yb–Cent2	129.3

Symmetry operator: (*) $1-x$, $-y$, $-z$.

[a] Cent = centroid of methylcyclopentadienyl ring

Table 2
Selected bond distances (Å) and angles (°) of complex **3**

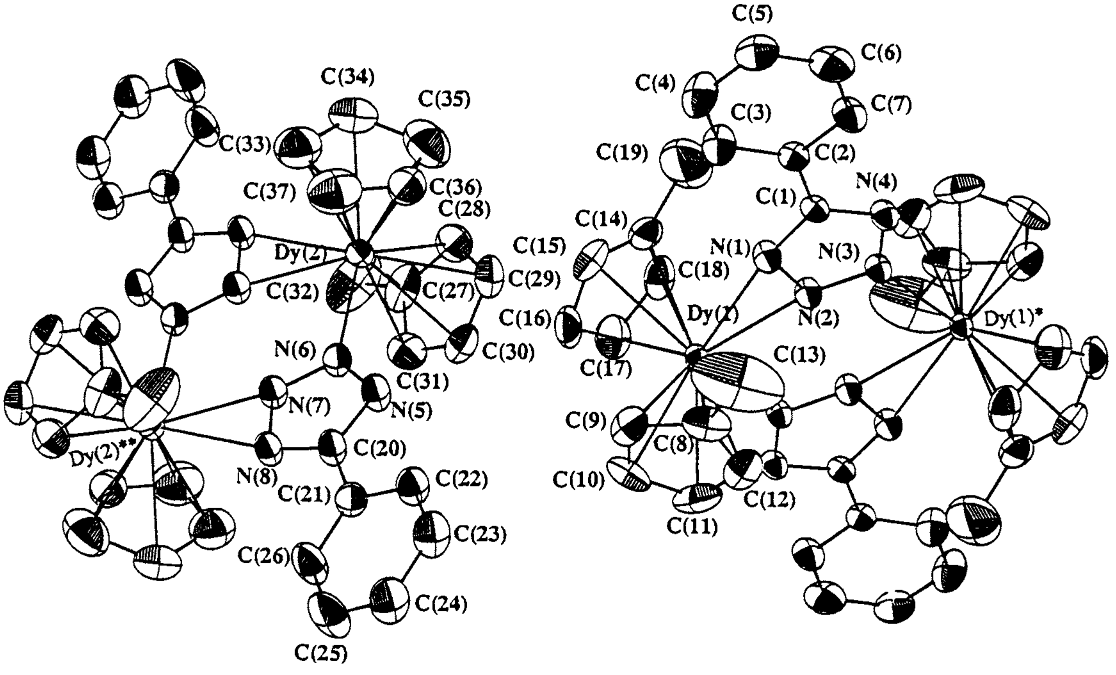
Dy(1)–C(8)	2.65(1)	Dy(1)–C(9)	2.59(1)
Dy(1)–C(10)	2.58(1)	Dy(1)–C(11)	2.58(1)
Dy(1)–C(12)	2.63(1)	Dy(1)–C(14)	2.63(1)
Dy(1)–C(15)	2.60(1)	Dy(1)–C(16)	2.59(1)
Dy(1)–C(17)	2.59(1)	Dy(1)–C(18)	2.64(1)
Dy(1)–Cent1[a]	2.334	Dy(1)–Cent2	2.335
Dy(1)–N(2)	2.360(6)	Dy(1)–N(3)*	2.470(6)
Dy(1)–N(1)	2.563(7)	N(1)–C(1)	1.34(1)
N(2)–N(3)	1.328(8)	N(3)–N(4)	1.334(1)
N(1)–N(2)	1.334(9)	N(4)–C(1)	1.35(1)
C(1)–C(2)	1.45(1)	Dy(1)–Dy(1)*	4.970(1)
Dy(2)–C(27)	2.65(1)	Dy(2)–C(28)	2.61(1)
Dy(2)–C(29)	2.58(1)	Dy(2)–C(30)	2.61(1)
Dy(2)–C(31)	2.61(1)	Dy(2)–C(33)	2.62(2)
Dy(2)–C(34)	2.59(1)	Dy(2)–C(35)	2.57(2)
Dy(2)–C(36)	2.59(1)	Dy(2)–C(37)	2.59(1)
Dy(2)–Cent3	2.344	Dy(2)–Cent4	2.311
Dy(2)–N(7)**	2.383(7)	Dy(2)–N(8)**	2.565(7)
Dy(2)–N(6)	2.471(7)	N(5)–C(20)	1.33(1)
N(5)–N(6)	1.34(1)	N(6)–N(7)	1.30(1)
N(8)–C(20)	1.33(1)	N(7)–N(8)	1.333(9)
C(20)–C(21)	1.46(1)	Dy(2)–DY(2)**	5.041(1)
N(2)–Dy(1)–N(3)*	78.0(2)	N(2)–Dy(1)–N(1)	31.1(2)
N(3)*–Dy(1)–N(1)	109.1(2)	N(3)–N(2)–DY(1)	167.2(5)
N(2)–N(3)–DY(1)*	114.7(4)	N(1)–C(1)–N(4)	110.3(7)
N(1)–N(2)–N(3)	109.8(6)	N(2)–N(3)–N(4)	108.9(6)
C(1)–N(1)–N(2)	105.4(6)	N(3)–N(4)–C(1)	105.6(6)
N(6)–Dy(2)–N(7)**	75.3(2)	N(6)–Dy(2)–N(8)**	106.3(2)
N(7)–Dy(2)**–N(8)	31.0(2)	N(7)–N(6)–DY(2)	116.9(5)
N(6)–N(7)–Dy(2)**	167.4(6)	N(5)–C(20)–N(8)	111.0(7)
N(5)–N(6)–N(7)	108.9(6)	N(6)–N(7)–N(8)	110.1(6)
C(20)–N(5)–N(6)	105.1(7)	N(7)–N(8)–C(20)	104.8(7)

Symmetry operator: (*) $+x$, $+y$, $+z$; (**) $-x$, $-y$, $-z$.

[a] Cent 1–4 represent the centroid of C(8)–C(12), C(14)–C(18), C(27)–C(31) and C(33)–C(37) ring, respectively.

Owing the steric effect of methyl group, the Dy(1)–C(8) and Dy(1)–C(14) distances are the longest, and the bond lengths for Dy to C(ring) far from the methyl group are the shortest. The bond lengths of Dy–C(ring) range from 2.58(1) to 2.65(1) Å and average 2.61(1) Å. The average value is smaller than those found in $[(C_5H_5)_2Dy(OCMe{=}CHCH_3)]_2$, average 2.668(6) Å [31]; $[(C_5H_4Me)Dy(PzMe_2)(OSiMe_2PzMe_2)]_2$, average 2.68(2) Å [28], and is similar to the value reported in $[(C_5H_5)_2DyCl]_\infty$, average 2.63(1) Å [32].

It is interesting to note that the structure of **3b** is similar to that of **3a** with the exception that two C_5H_5 groups replace two C_5H_4Me ones. The bond lengths of Dy(2)–C(C_5H_5) range from 2.57(2) to 2.62(2) Å [average 2.59(2) Å], Dy(2)–C(C_5H_4Me) from 2.58(1) to 2.65(1) Å [average 2.61(1) Å], which are in normal range of Dy–C(η^5) bond observed. The D(2)–N bond lengths are comparable to the corresponding values in **3a**. Significantly, since **3b** contains two different cyclopentadienyl rings, in **3b** the coplanarity between two Dy atoms and two tetrazolate rings is not as well as



(3b) **(3a)**

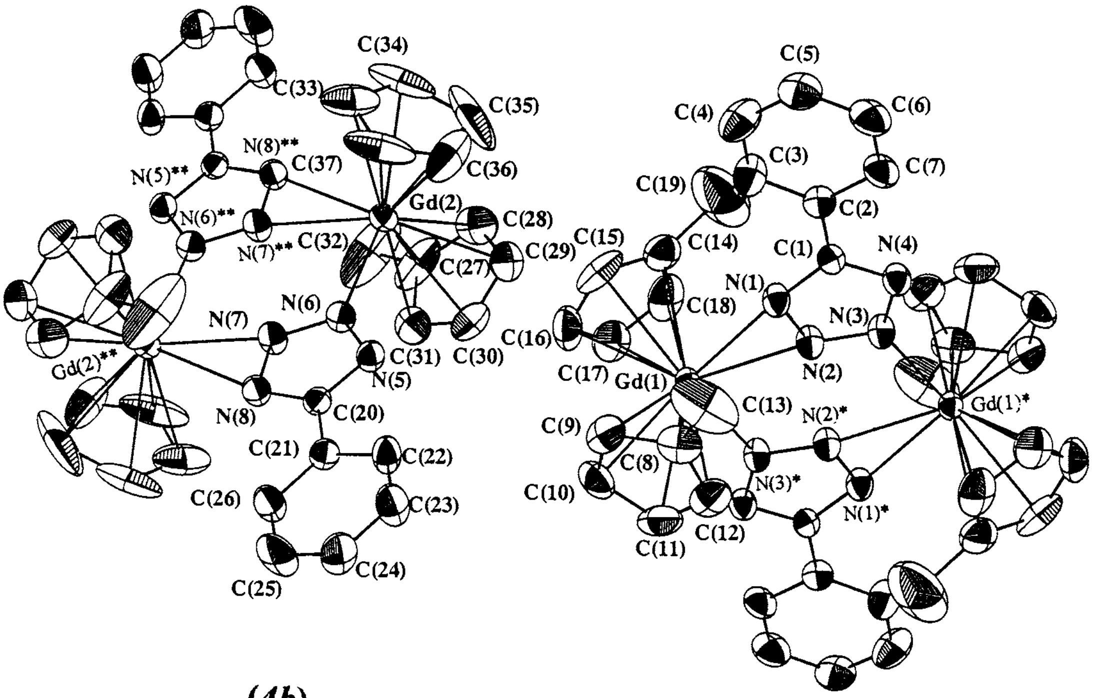
Fig. 2. Molecular structure of [{(C_5H_4Me)(C_5H_5)DyTz}$_2$][{(C_5H_4Me)$_2$DyTz}$_2$].

those in **3a** and **1**, and the Dy(2)–Dy(2)** distance of 5.041(1) Å is slightly longer than that of Dy(1)–Dy(1)*, 4.970(1) Å.

2.4. Crystal structure of [{(C_5H_4Me)(C_5H_5)-Gd(μ-η^1:η^2-Tz)}$_2$][{(C_5H_4Me)$_2$Gd(μ-η^1:η^2-Tz)}$_2$] (4)

The structure of **4** is shown in Fig. 3. There are also two disconnected structural units crystallizing in one asymmetrical unit, each of which consists of two gadolinium atoms bridged by two 5-phenyltetrazolate ligands. These tetrazolate ligands are of the η^3-type, with the nitrogen atoms at 1, 2 and 3-position talking part in bonding. The edge-bridged tetrahedral geometry about each gadolinium atom is completed by three N atoms of Tz ligands and two centroids of five-membered rings of C_5H_4Me or C_5H_5 group. The structural parameters of **4** (Table 3) are very similar to those for complex **3**. The ranges of Gd–C(ring) values in the two parts are nearly the same, 2.58(1)–2.69(1) Å in [(C_5H_4Me)$_2$Gd(μ-η^1:η^2-Tz)]$_2$ (**4a**) and 2.59(2)–2.70(1) Å in [(C_5H_4Me)(C_5H_5)Gd(μ-η^1:η^2-Tz)]$_2$ (**4b**), and the Gd–C(ring) averages coincide at 2.64(1) Å, despite the differences in ring substitution. The average Gd–C distances for both the C_5H_5 and C_5H_4Me rings [2.64(1) and 2.64(1) Å] are slightly shorter than those observed in other (cyclopentadienyl)gadolinium complexes: [(C_5H_5)$_2$Gd(μ-η^2-ONCMe$_2$)]$_2$, 2.68(2) Å [14], (C_5H_5)GdCl$_2$(THF)$_3$, 2.68 Å [33], and [(C_5H_5)$_2$GdCl]$_4$, 2.67(1) Å [34]. The angular parameters (Table 3) in **4a** and **4b** are also similar. Examinations of the Gd–N distances in **4** show that when the differences in metallic radii are subtracted [30], all the Gd–N lengths in **4** are reasonable in comparison with the corresponding values in the isostructural complex **3**. The Gd–N(donating) distances of 2.566(8) and 2.593(7) Å are similar to those found in [Gd($C_{26}H_{30}N_6$)(H_2O)$_3$]Cl$_3$ · 3H_2O, 2.57(1)–2.69(1) Å [35].

It has been reported that the complexes containing two metals bridged by two azolate groups generally exist in boat conformations [9,10]. However, from Table 4 it can be seen that the bridging unit Ln$_2$N$_6$ is planar in complexes **1**, **3** and **4**. All the dihedral angles between the phenyl group and the tetrazolate ring are smaller than 14°, favoring orbital conjugation between the two cycles. This was also observed in the IR spectra, in which the skeletal stretch at 1562 cm^{-1} for phenyl ring of TzH is shifted to lower frequency at ca. 1522 cm^{-1} for complexes **1**–**4**, and would explain the short C–C distance of 1.44–1.48 Å between phenyl and tetrazolate ring. The C–N and N–N distances of tetrazolate ring for each of complexes are the approximately equivalent, and are significantly shorter than the corresponding C–N and N–N single-bond distances, respectively, indicating partial double bond character. In other words, the π-electrons of the tetrazolate ring in



(4b)

(4a)

Fig. 3. Molecular structure of $[\{(C_5Me)(C_5H_5)GdTz\}_2][\{(C_5H_4Me)_2GdTz\}_2]$.

the present three structures are delocalized over the ring. This is in contrast to the previously reported results for $Cu_2(N_4CCF_3)_2[(CH_2PPh_2)_2]_3$ [36] and $Ag_2(PPh_3)_4(N_4CCF_3)_2$ [37], where the π-electron density is localized in the nitrogen atoms at the 2- and 3-positions of the tetrazolate ring [N–N, 1.12 Å].

In conclusion, reaction of 5-phenyl-1H-tetrazole with $(C_5H_4Me)_3Ln$ gave the 2- and 3-positions tetrazolate bridging complexes with donating coordination of 1-position instead of the 1-position σ-bonding ones, it demonstrated clearly that the tetrazolate anion is fluxional about the bonding of Ln^{3+} to nitrogen atom, and the steric factors favor the nitrogen atoms at 2- and 3-positions to coordinate to metal ions. Furthermore, although the π-electrons of the tetrazolate ring in complexes **1**–**4** are delocalized over the ring, as evidenced by the approximately equal lengths observed for C=N and N=N bonds and by IR spectrum, in the solid state the 5-phenytetrazolate group is bonded to Ln^{3+} ions in η^3-fashion other than in η^5-fashion.

The most important feature about the three structures is the presence of chelating coordination for the 5-phenyltetrazolate group. So far, the structures of only two complexes, namely $Rh_3(\mu_3\text{-}N_4CH)(\mu\text{-}Cl)Cl(COD)(CO)_2$ and $Rh_3(\mu_3\text{-}N_4CH)(\mu\text{-}Cl)Cl(CO)_6$, do the data indicate that the tetrazolate group acts as a tridentate ligand [12]. But both structures have the following common features different from the title structures: (a) the tetrazolate group is $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$ fashion coordinated to three metal centers through the nitrogen atoms at the 1-, 2- and 4-positions, in which there is relatively small crowding of the coordination sphere resulting from steric interaction between three coordination centers; (h) the three M–N bond distances are almost equivalent; (c) there is not the bulky substituent at the 5-position of the tetrazolate ring. On the other hand, the previous structure determinations of complexes containing 5-phenyltetrazolate anions show that in all cases it is monodentate and that the site of coordination is at 2-position [11]. Structures involving bridging the least sterically hindered 2- and 3-positions of the 5-aryl-tetrazolate ligands are only proposed for a few complexes based mainly on spectroscopic data and the conclusions derived are mostly tentative [38,39]. Thus, the structures of complexes **1**, **3** and **4** are unique among the tetrazolate organometallic complexes. This novel mode of coordination is apparently the result of the tendency of the large ionic radius Ln^{3+} to attain higher coordination number. So the donating coordination for Ln^{3+} to N atom at 1-position of 5-phenyltetrazolate should be enhanced with Ln^{3+} radii increasing.

Table 3
Selected bond distances (Å) and angles (°) of complex **4**

Gd(1)–C(8)	2.69(1)	Gd(1)–C(9)	2.63(1)
Gd(1)–C(10)	2.58(1)	Gd(1)–C(11)	2.65(1)
Gd(1)–C(12)	2.67(1)	Gd(1)–C(14)	2.66(1)
Gd(1)–C(15)	2.59(1)	Gd(1)–C(16)	2.64(1)
Gd(1)–C(17)	2.65(1)	Gd(1)–C(18)	2.66(1)
Gd(1)–Cent1[a]	2.361	Gd(1)–Cent2	2.383
Gd(1)–N(2)	2.409(7)	Gd(1)–N(3)*	2.498(7)
Gd(1)–N(1)	2.566(8)	Gd(1)–Gd(1)*	5.016(2)
N(1)–C(1)	1.38(1)	N(2)–N(3)	1.32(1)
N(3)–N(4)	1.34(1)	N(4)–C(1)	1.36(1)
N(1)–N(2)	1.33(1)	C(1)–C(2)	1.44(1)
Gd(2)–C(27)	2.70(1)	Gd(2)–C(33)	2.66(1)
Gd(2)–C(28)	2.64(1)	Gd(2)–C(34)	2.64(2)
Gd(2)–C(29)	2.63(1)	Gd(2)–C(35)	2.59(2)
Gd(2)–C(30)	2.63(1)	Gd(2)–C(36)	2.64(2)
Gd(2)–C(31)	2.65(2)	Gd(2)–C(37)	2.62(2)
Gd(2)–Cent3	2.377	Gd(2)–Cent4	2.357
Gd(2)–N(8)**	2.593(7)	Gd(2)–N(6)	2.500(8)
Gd(2)–N(7)**	2.406(7)	N(5)–C(20)	1.33(1)
N(5)–N(6)	1.34(1)	N(6)–N(7)	1.32(1)
N(8)–C(20)	1.33(1)	N(7)–N(8)	1.34(1)
C(20)–C(21)	1.45(1)	Gd(2)–Gd(2)**	5.079(2)
N(2)–Gd(1)–N(3)*	77.9(2)	N(2)–Gd(1)–N(1)	30.8(2)
N(3)*–Gd(1)–N(1)	108.6(2)	N(3)–N(2)–Gd(1)	168.6(6)
N(2)–N(3)–Gd(1)*	113.4(6)	N(1)–C(1)–N(4)	108.3(8)
N(1)–N(2)–N(3)	110.1(7)	N(2)–N(3)–N(4)	109.2(7)
N(2)–N(1)–C(1)	106.0(7)	N(3)–N(4)–C(1)	106.4(1)
N(6)–Gd(2)–N(7)**	75.8(3)	N(6)–Gd(2)–N(8)**	106.4(2)
N(7)–Gd(2)**–N(8)	30.7(2)	N(7)–N(6)–Gd(2)	115.8(5)
N(6)–N(7)–Gd(2)**	166.1(7)	N(5)–C(20)–N(8)	110.7(8)
N(5)–N(6)–N(7)	109.4(7)	N(6)–N(7)–N(8)	108.9(7)
N(7)–N(8)–C(20)	105.5(7)	C(20)–N(5)–N(6)	105.4(7)

Symmetry operator: (*) $+x$, $+y$, $+z$; (**) $-x$, $-y$, $-z$.
[a] Cent 1–4 represents the centroid of C(8)–C(12), C(14)–C(18), C(27)–C(31) and C(33)–C(37), respectively.

3. Experimental section

3.1. Materials and instrumentation

The title complexes are extremely air and moisture sensitive. Therefore all the manipulations were carried out under purified argon using Schlenk technique with rigorous exclusion of air and moisture. All solvents were refluxed and distilled over sodium benzophenone ketyl immediately before use. $(C_5H_4Me)_3Ln$ (Ln = Gd, Dy, Er, Yb) were prepared from NaC_5H_4Me and anhydrous $LnCl_3$ as described in the literature [40], and the methylcyclopentadiene was purified by fractional distillation. Analytical grade 5-phenyl-1H-tetrazole (Aldrich) was used without further purification. Elemental analyses for carbon, hydrogen and nitrogen were performed on a Rapid CHN-O analyzer. Metal analyses for lanthanides were accomplished on a Jarrell-Ash 1100 + 2000 ICP quantometer or using the literature method [41]. Infrared spectra were obtained on a NICOLE FT–IR SDX spectrometer. A Nujol mull of the complex was pressed between KBr pellets. Mass spectra were recorded on a HP5989A instrument operating in EI mode at a resolving power of 1000. The crystal samples were introduced by direct probe inlet without any heating. The ion source temperature was 200°C. ^{1}H-NMR spectra were recorded with a Bruker MSL-300 MHz spectrometer and referenced to residual aryl protons in C_6D_6 (δ 7.40)

3.2. Syntheses of $[(C_5H_4Me)_2LnTz]_2$ (Ln = Yb, Er)

$Yb(C_5H_4Me)_3$ (0.34 g, 0.83 mmol) and 5-phenyl-1H-tetrazole (TzH) (0.12 g, 0.83 mmol) were mixed in 20 ml of tetrahydrofuran (THF) and allowed to stir at room temperature for 36 h. Then the solution was concentrated under reduced pressure to ca. 3 ml. A number of needle red crystals were obtained by diffusing slowly *n*-hexane into it. Complex 2 was synthesized by using the same produce.

3.3. Synthesis of $[\{(C_5H_4Me)(C_5H_5)DyTz\}_2][\{(C_5H_4Me)_2DyTz\}_2]$ (**3**)

A 15 ml of THF was added to a mixture of $(C_5H_4Me)_3Dy$ (0.387 g, 0.97 mmol) and TzH (0.142 g, 0.97 mmol) and the reaction was stirred overnight. The resulting solution was concentrated under reduced pressure to ca. 3 ml. The crystals isolated from this mixture by diffusing slowly *n*-hexane into it were identified as $[\{(C_5H_4Me)(C_5H_5)DyTz\}_2][\{(C_5H_4Me)_2DyTz\}_2]$ (**3**), which implied that there is a small amount of $(C_5H_4Me)_2Dy(C_5H_5)$ in the used $(C_5H_4Me)_3Dy$, as defined latterly by ^{1}H-NMR and MS spectra. Presumably $(C_5H_4Me)_2Dy(C_5H_5)$ may result from the presence of a little cyclopentadiene in methylcyclopentadiene.

3.4. Synthesis of $[\{(C_5H_4Me)(C_5H_5)GdTz\}_2][\{(C_5H_4Me)_2GdTz\}_2]$ (**4**)

TzH (0.076 g, 0.52 mmol) and $(C_5H_4Me)_3Gd$ (0.205 g, 0.52 mmol) were mixed in 20 ml of toluene. After stirring for 48 h at ambient temperature, the resulting mixture was centrifuged. The solution was cooled in − 18°C and gave also 1:1 complex $[\{(C_5H_4Me)(C_5H_5)GdTz\}_2][\{(C_5H_4Me)_2GdTz\}_2]$ (**4**) as the only crystal product as observed above.

$[(C_5H_4Me)_2YbTz]_2$ (**1**): red, yield, 78%. Elemental Anal.: Found: C, 47.25; H, 4.06; N, 11.88; Yb, 36.25. $C_{19}H_{19}N_4Yb$ Calcd: C, 47.90; H, 4.02; N, 11.75; Yb, 36.32. Spectroscopic data: IR (KBr, cm^{-1}): 3065m, 2730m, 2672m, 1606w, 1581m, 1522m, 1459s, 1447s, 1378s, 1353m, 1306m, 1278m, 1234m, 1159m, 1116w, 1072m, 1047m, 1028m, 1006, 971w, 931m, 887m, 846m,

Table 4
The equations of the best planes and atomic deviations (Å)

Planes equations, atoms and their deviations							
$[(C_5H_4Me)_2YbTz]_2$							
$P1$ $1.532x+0.6373y-1.218z=0.7657$							
Yb	N(1)	N(2)	N(3)	N(4)	C(1)		
0.0000	0.0477	−0.0010	−0.0451	0.0332	−0.0356		
Yb*	N(1)*	N(2)*	N(3)*	N(4)*	C(1)*		
0.0000	−0.0470	0.0010	0.0451	−0.0332	0.0356		
$[\{(C_5H_4Me)(C_5H_5)DyTz\}_2][\{(C_5H_4Me)_2DyTz\}_2]$							
$P1$ $0.6517x+10.36y-0.1653z=0.4351$							
Dy(1)	N(1)	N(2)	N(3)	N(4)	C(1)		
−0.0002	−0.0329	−0.0165	0.0226	0.0254	0.0109		
Dy(1)*	N(1)*	N(2)*	N(3)*	N(4)*	C(1)*		
0.0002	0.0330	0.0165	−0.0226	−0.0254	−0.0109		
$P2$ $0.6570x-0.699y+0.455z=-0.113\times10^{-6}$							
Dy(2)	N(6)	N(7)	N(8)	N(6)**	N(7)**	N(8)**	Dy(2)**
0.0000	0.0274	−0.0269	−0.0052	−0.0274	0.0269	0.0052	0.0000
$[\{(C_5H_4Me)(C_5H_5)GdTz\}_2][\{(C_5H_4Me)_2GdTz)\}]$							
$P1$ $0.650x+10.6y-0.165z=0.447$							
Gd(1)	N(1)	N(2)	N(3)	N(4)	C(1)		
−0.0004	0.0009	−0.0086	0.0179	0.0161	0.0078		
Gd(1)*	N(1)*	N(2)*	N(3)*	N(4)*	C(1)*		
0.0004	−0.0009	0.0086	−0.0179	−0.0161	−0.0078		
$P2$ $0.681x-0.670y+0.464z=-0.452\times10^{-6}$							
Gd(2)	N(6)	N(7)	N(8)	N(6)**	N(7)**	N(8)**	Gd(2)**
0.0000	0.0524	−0.0756	−0.0036	−0.0524	0.0757	0.0036	0.0000

831m, 775s, 728s, 691s, 628w, 506w, 456w. MS(EI): m/z (fragment, relative intensity %) = 954 (M, 3.9), 875 (M-Cp′, 12.6), 808 (M-TzH, 10.3), 796 (M-2Cp′, 2.8), 771 (M-Cp′H-PhCN, 15.2), 743 (M + 3-Cp′H-PhCN-N_2, 3.7), 729 (M-Cp′-TzH, 6.7), 668 (M-Cp′H-2PhCN, 8.5), 546 (M-2Cp′H-PhCN-Tz, 11.9), 477 (M/2, 1.1), 464 (Yb(Tz)$_2$, 0.9), 411 (Cp'_3Yb,$Cp'_2Yb \rightarrow Cp'_2Yb$; 41.3), 253 (Cp′Yb, 100), 174 (Yb, 19.1), 103 (PhCN, 22.1), 79 (Cp′, 35.5) (Cp′ = $C_5H_4CH_3$).

$[(C_5H_4Me)_2Er(\mu\text{-}Tz)]_2$ (**2**): pale-red, yield, 60%. Elemental Anal.: Found: C, 48.10; H, 4.18; N, 12.12; Er, 35.76. $C_{19}H_{19}N_4Er$ Calcd: C, 48.49; H, 4.07; N, 11.90; Er, 35.54. Spectroscopic data: IR (KBr, cm^{-1}): 3062m, 2730m, 2672w, 1603w, 1582w, 1522m, 1440s, 1378s, 1352m, 1306m, 1279m, 1233m, 1157m, 1115w, 1069m, 1048m, 1031m, 1009s, 931m, 887m, 846m, 832m, 777s, 729s, 691s, 628w, 506w, 456w. MS(EI): m/z (fragment, relative intensity %) = 941 (M + 3, 0.9), 862 (M + 3-Cp′, 2.0), 795 (M + 3-TzH, 1.5), 758 (M + 3-Cp′H-PhCN, 3.2), 730 (M + 3-Cp′H-PhCN-N2, 1.8), 716 (M + 3-Cp′-TzH, 0.2), 655 (M + 3-Cp′H-2PhCN, 2.3), 601 (Er(Tz)3, 0.8), 403 (Cp'_3Er, 4.5), 324 (Cp'_2Er, 90.2), 245 (Cp′Er, 35.6), 166 (Er, 9.6), 103 (PhCN, 44.9), 79 (Cp′, 100).

$[\{(C_5H_4Me)(C_5H_5)DyTz\}_2][\{(C_5H_4Me)_2DyTz\}_2]$ (**3**): yellow, yield, 60%. Elemental Anal.: Found: C, 47.40; H, 4.03; N, 12.56; Dy, 35.67. $C_{37}H_{36}N_8Dy_2$ Calcd: C, 48.42; H, 3.95; N, 12.21; Dy, 35.41. Spectroscopic data: IR (KBr, cm^{-1}): 3051m, 2730m, 2672m, 1609, 1584m, 1525w, 1447s, 1378s, 1352m, 1306m, 1278m, 1231m, 1168m, 1150m, 1118w, 1072m, 1047m, 1031m, 1009m, 972w, 931m, 887m, 831m, 771s, 731s, 693s, 625w, 562w, 506w, 459w. MS(EI): m/z (fragment, relative intensity %) = 934 (M, 1.4), 855 (M-Cp′, 8.5), 841 (M′-Cp, 1.8), 827 (M′-Cp′, 1.9), 788 (M-TzH, 10.6), 776 ([M-2Cp′]/[M′-2Cp], 1.9), 748 (M′-2Cp′, 5.2), 751 (M-Cp′H-PhCN, 11.6), 737 (M′-CpH-PhCN, 2.0), 723 (M′-Cp′H-PhCN, 4.1), 709 (M-Cp′H-Tz, 1.1), 681 (M′-Cp′H-Tz, 1.0), 648 (M-Cp′H-2PhCN, 5.2), 634 (M′-CpH-2PhCN, 1.2), 600 (M′-2Cp′H-TzH, 1.3), 599 [Dy(Tz)$_3$, 1.8], 454 (Dy(Tz)$_2$, 0.8), 526 (M-2Cp′H-PhCN-Tz, 0.8), 498 (M′-2Cp′HPhCN-Tz, 13.7), 467 (M/2, 1.8), 453 (M′/2, 1.2), 401 (Cp'_3Dy, 6.3), 387 (Cp'_2DyCp, 7.6), 322 (Cp'_2Dy, 100), 308 (CpCp′Dy, 12.3), 294 [Cp_2Dy, 2.8], 243 (Cp′Dy, 21.8), 229 (CpDy, 6.9), 164 (Dy, 14.9), 103 (PhCN, 37.4), 79 (Cp′, 24.8), 65 (Cp, 3.0) (Cp = C_5H_5, M′ = $[(C_5H_4Me)(C_5H_5)DyTz]_2$, M = $[(C_5H_4Me)_2Dy\text{-}Tz]_2$).

$[\{(C_5H_4Me)(C_5H_5)GdTz\}_2][\{(C_5H_4Me)_2GdTz\}_2]$ (**4**): colorless, yield, 50%. Elemental Anal: Found: C, 48.56; H, 4.03; N, 12.17; Gd, 34.24. $C_{37}H_{36}N_8Gd'$ Calcd: C, 48.98; H, 4.00; N, 12.35; Gd, 34.67. Spectroscopic data: IR(KBr, cm^{-1}): 3065m, 2730m, 1603w, 1546w, 1522w, 1447s, 1378s, 1350m, 1306w, 1278w, 1228m, 1172m, 1147m, 1112w, 1069m, 1044m, 1028m, 1006s, 931m, 896w, 853w, 828m, 769s, 728s, 691s, 625m, 506w, 462m. MS(EI): m/z (fragment, relative intensity %) = 922 (M,

Table 5
Crystal and data collection parameters of complexes **1**, **3** and **4**

Formula	$C_{38}H_{38}N_8Yb_2$	$C_{74}H_{72}N_{16}Dy_4$	$C_{74}H_{72}N_{16}Gd_4$
Molecular weight	952.86	1935.48	1814.48
Crystal color	Red	Yellow	Colorless
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c* (#15)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
Lattice parameters			
a (A)	25.596(2)	9.374(2)	9.420(4)
b (A)	8.342(1)	13.048(2)	13.215(4)
c (°)	21.573(2)	16.542(4)	16.677(5)
α (°)		86.95(2)	87.24(2)
β (°)	129.322(9)	74.61(1)	74.50(3)
γ (°)		77.31(1)	77.08(3)
V (Å^3)	3563.5(8)	1902.9(9)	1950(1)
Z	4	1	1
Dc (g cm^{-3})	1.776	1.602	1.545
F(000)	1848	892	884
Radiation	Mo K$_\alpha$ (0.71069 Å)	Mo K$_\alpha$(0.71069 Å)	Mo K$_\alpha$(0.71069 Å)
μ (mm)	5.240	3.966	3.421
Scan width (°)	0.50+0.35 tan θ	0.85+0.35 tan θ	0.60+0.35 tan θ
Scan speed (° min^{-1})	<5.49	<5.49	<5.49
hkl range	−30–30, 0–9, 0–25	0–11, −15–15, −19–19	0–11, −15–15, −19–19
$2\theta_{max}$ (°)	50	50	50
No. of reflections measured	3444	6657	6856
No. of unique reflections	3383	5363	5145
No. of reflections observed	2700	5349	5117
[I>3σ(I)]			
No. of variables	217	424	424
R	0.031	0.046	0.051
R_ω	0.041	0.059	0.064
w	$1/\sigma^2$ (F)	$1/\sigma^2$ (F)	$1/\sigma^2$ (F)
S	1.21	1.75	1.71
$(\Delta/\sigma)_{max}$	0.003	0.009	0 003
$\Delta\rho_{max}$ (e Å^{-3})	0.95	1.21	1.30

1.1), 843 (M-Cp′, 6.6), 829 (M′-Cp, 1.2), 815 (M′-Cp′, 1.2), 776 (M-TzH, 3.8), 764 ([M-2Cp′]/[M′-2Cp], 1.5), 736 (M′-2Cp′, 4.0), 739 (M-Cp′H-PhCN, 7.7), 725 (M′-CpH-PhCN, 1.2), 711 (M′Cp′H-PhCN, 2.2), 636 (M-Cp′H-2PhCN, 3.0), 622 (M′-CpH-2PhCN, 1.2), 593 [Tz_3Gd, 1.0], 588 (M′-2Cp′H-TzH, 1.0), 514 (M-2Cp′H-PhCN-Tz, 1.0), 486 (M′-2Cp′H-PhCN-Tz, 11.53) 461 (M/2, 3.8), 395 (Cp$'_2$CpGd, 6.4), 316 (Cp′2Gd, 100), 302 (CpCp′Gd, 12.2), 288 [Cp_2Gd, 3.0], 237 (Cp′Gd, 11.6), 223 (CpGd, 3.9), 158 (Gd, 1.2), 103 (PhCN, 22.8), 79 (Cp′, 32.2), 65 (Cp, 5.1) (M′ = [(C_5H_4Me)(C_5H_5)GdTz]$_2$, M = [(C_5H_4Me)$_2$GdTz]$_2$).

*3.5. X-ray crystallography of [($C_5H_4CH_3$)$_2$Yb-(μ-η^1:η^2-Tz)]$_2$ (**1**)*

A single crystal of **1** measuring approximately 0.45 × 0.30 × 0.25 mm was sealed under N_2 in a thin-walled glass capillary. Data were collected on an Enraf–Nonius CAD-4 diffractometer at 296 K, using graphite-monochromated Mo K$_\alpha$ radiation ($\lambda = 0.71069$ Å), ω–2θ scan mode. Accurate cell parameters were obtained by the least-squares refinement of the setting angles of 25 reflections with $13.10 < \theta < 14.87°$. Intensities were corrected for Lorentz-polarization effects and empirical absorption. The structure was solved by the heavy-atom method using the TEXSAN program [42] and Fourier techniques, refined on *F*, 217 parameters. Crystal and data collection parameters are given in Table 5. Atomic coordinates and equivalent thermal parameters of all the non-hydrogen atoms are listed in Table 6.

*3.6. X-ray crystallography of [{(C_5H_4Me)(C_5H_5)Dy(μ-η^1:η^2-Tz)}$_2$] [{(C_5H_4Me)$_2$Dy(μ-η^1:η^2-Tz)}$_2$] (**3**)*

A single crystal measuring 0.55 × 0.40 × 0.36 mm was sealed under argon in a thin-walled glass capillary and mounted on a Enraf–Nonius CAW4 diffractometer. Lattice parameters were determined from the angular settings of 25 reflections with $12.99 < \theta < 13.87°$. Crystal and data collection parameters are given in Table 5. The intensities were corrected for lorentz, polarization and absorption effects. A combination of direct methods and difference Fourier techniques provided the locations of all non-hydrogen atoms which were refined with anisotropic temperature parameters by the use of full-matrix least-squares methods. The H-atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in the refinement. The final difference Fourier showed the presence of few badly disordered THF crystallization in the lattice, but the positions of these atoms were not refined. All calculations were performed on a Micro VAX 3100 computer. Atomic coordinates and equivalent thermal parameters of all the non-hydrogen atoms are listed in Table 7.

3.7. X-ray crystallography of $[\{(C_5H_4Me)(C_5H_5)Gd(\mu\text{-}\eta^1{:}\eta^2\text{-}Tz)\}_2]$ $[\{(C_5H_4Me)_2Gd(\mu\text{-}\eta^1{:}\eta^2\text{-}Tz)\}_2]$ *(4)*

A single crystal measuring 0.80 × 0.60 × 0.10 mm was handled as described above for **3**. Lattice parameters were determined from 25 computer-centred reflections with $12.99 < \theta < 14.92°$. Crystal and data collection parameters are given in Table 5. A combination of direct methods (MITHRIL) and difference Fourier techniques provided the locations of all non-hydrogen atoms which were refined with anisotropic temperature parameters by the of full-matrix least-squares methods. No hydrogen atoms were located. The final difference Fourier maps showed the presence of relatively few amount of disordered solvate molecules in the lattice which could not be completely resolved. Atomic coordinates and equivalent thermal parameters of all the non-hydrogen atoms are listed in Table 8.

Table 6
Atomic coordinates and equivalent thermal parameters for complex **1**

Atom	*x*	*y*	*z*	*B* (eq)
Yb	0.592274(11)	0.04897(3)	0.141591(13)	3.59(1)
N(1)	0.4816(2)	0.1146(7)	0.0328(3)	4.5(2)
N(2)	0.4231(2)	0.1092(6)	−0.0391(3)	4.0(2)
N(3)	0.3792(2)	0.2029(6)	−0.0419(3)	4.0(2)
N(4)	0.4778(2)	0.2110(6)	0.0796(3)	4.8(2)
C(1)	0.4142(2)	0.2624(7)	0.0323(3)	3.6(2)
C(2)	0.3852(3)	0.3727(7)	0.0567(3)	4.1(2)
C(3)	0.4274(4)	0.4563(8)	0.1286(4)	5.5(3)
C(4)	0.3983(5)	0.5582(10)	0.1510(5)	7.2(4)
C(5)	0.3304(5)	0.5708(11)	0.1045(6)	7.8(4)
C(6)	0.2898(5)	0.4876(13)	0.0346(7)	8.6(4)
C(7)	0.3165(4)	0.3892(10)	0.0091(5)	6.2(3)
C(8)	0.6032(4)	0.0361(9)	0.2640(5)	5.2(3)
C(9)	0.5415(3)	−0.1031(9)	0.1968(4)	5.3(3)
C(10)	0.5561(4)	−0.2194(8)	0.1637(4)	5.3(3)
C(11)	0.6255(4)	−0.2281(8)	0.2095(4)	5.6(3)
C(12)	0.6547(3)	−0.1181(10)	0.2704(4)	5.4(3)
C(13)	0.6112(6)	0.0856(14)	0.3194(6)	9.2(5)
C(14)	0.6550(3)	0.2207(9)	0.1055(4)	5.7(3)
C(15)	0.6220(4)	0.3293(8)	0.1183(5)	6.4(3)
C(16)	0.6495(5)	0.3232(11)	0.1978(6)	7.6(4)
C(17)	0.7015(5)	0.2097(15)	0.2355(5)	8.7(5)
C(18)	0.7042(4)	0.1418(11)	0.1780(6)	7.0(4)
C(19)	0.6450(6)	0.2012(15)	0.0296(7)	10.8(6)

Table 7
Positional parameters and *B* (eq) for complex **3**

Atom	*x*	*y*	*z*	*B* (eq)
Dy(1)	0.13051(4)	0.39695(3)	0.36908(2)	3.37(2)
Dy(2)	−0.11059(4)	−0.00207(3)	0.15643(2)	4.14(3)
N(1)	0.2418(7)	0.3438(5)	0.4947(4)	4.4(4)
N(2)	0.1215(7)	0.4236(5)	0.5105(4)	4.2(4)
N(3)	0.0932(7)	0.4577(5)	0.5885(4)	3.7(4)
N(4)	0.1948(7)	0.3998(5)	0.6249(4)	4.2(4)
N(5)	0.1487(10)	0.1586(7)	0.0657(4)	6.3(6)
N(6)	0.0629(8)	0.0922(6)	0.0569(4)	5.0(5)
N(7)	0.0880(8)	0.0719(6)	−0.223(4)	4.9(5)
N(8)	0.1830(9)	0.1283(6)	−0.0681(4)	5.4(5)
C(1)	0.2875(8)	0.3306(6)	0.5656(4)	3.6(5)
C(2)	0.4157(8)	0.2517(6)	0.5769(5)	4.0(5)
C(3)	0.4901(11)	0.1738(8)	0.5180(7)	6.3(7)
C(4)	0.6111(13)	0.1008(9)	0.5294(8)	7.7(9)
C(5)	0.6609(12)	0.1031(9)	0.6023(8)	6.9(8)
C(6)	0.5889(13)	0.1794(10)	0.6605(7)	7.4(9)
C(7)	0.4676(11)	0.2519(8)	0.6483(6)	5.8(7)
C(8)	0.3837(113)	0.4639(12)	0.3220(8)	7(1)
C(9)	0.3785(13)	0.4015(9)	0.2540(8)	7.4(8)
C(10)	0.2651(16)	0.4587(13)	0.2240(7)	8(1)
C(11)	0.2036(16)	0.5469(11)	0.2692(11)	9(1)
C(12)	0.2753(15)	0.5505(10)	0.3261(9)	8(1)
C(13)	0.507(3)	0.440(3)	0.3720(18)	23(3)
C(14)	0.0379(16)	0.2215(9)	0.4155(7)	6.5(9)
C(15)	0.1484(14)	0.1991(8)	0.3444(10)	8(1)
C(16)	0.0868(19)	0.2549(11)	0.2805(7)	8(1)
C(17)	−0.0531(17)	0.3103(11)	0.317S(9)	8(1)
C(18)	−0.0833(14)	0.2869(10)	0.4018(8)	7(1)
C(19)	0.031(3)	0.1810(18)	0.5005(13)	20(3)
C(20)	0.2215(11)	0.1791(8)	−0.0122(5)	5.7(7)
C(21)	0.3296(12)	0.2481(8)	0.0341(6)	6.0(7)
C(22)	0.3843(12)	0.2833(9)	0.0270(6)	6.5(8)
C(23)	0.4870(14)	0.3467(11)	0.0078(8)	8(1)
C(24)	0.5297(17)	0.3808(11)	0.0748(9)	10(1)
C(25)	0.473(2)	0.3492(13)	−0.1350(8)	12(2)
C(26)	0.3717(16)	0.2818(11)	−0.1147(6)	9(1)
C(27)	−0.4028(11)	0.0822(10)	0.1777(9)	7(1)
C(28)	−0.3752(14)	0.0764(10)	0.2557(8)	8(1)
C(29)	−0.2846(14)	0.1426(10)	0.2599(8)	7(1)
C(30)	−0.2564(14)	0.1927(8)	0.1862(9)	7.2(9)
C(31)	−0.3219(14)	0.1553(10)	0.1335(8)	8(1)
C(32)	−0.507(2)	0.0346(15)	0.1406(16)	15(2)
C(33)	0.080(2)	−0.1766(14)	0.1735(12)	11(2)
C(34)	−0.0413(18)	−0.1627(13)	0.2481(10)	10(1)
C(35)	−0.034(2)	−0.0665(17)	0.2914(11)	13(2)
C(36)	0.0939(17)	−0.0400(10)	0.2398(9)	8(1)
C(37)	0.153(2)	−0.0976(17)	0.1718(13)	12(2)

Table 8
Positional parameters and *B* (eq) for complex **4**

Atom	*x*	*y*	*z*	*B* (eq)
Gd(1)	0.13511(5)	0.39659(3)	0.36908(2)	3.93(3)
Gd(2)	−0.10900(5)	−0.00230(4)	0.15660(3)	4.33(3)
N(1)	0.2438(9)	0.1497(6)	0.4949(5)	5.0(5)
N(2)	0.1217(8)	0.4264(6)	0.5124(5)	4.8(5)
N(3)	0.0928(8)	0.4587(6)	0.5898(5)	4.7(5)
N(4)	0.1951(9)	0.4014(6)	0.6258(5)	4.9(5)
N(5)	0.1433(9)	0.1627(6)	0.0651(5)	5.0(6)
N(6)	0.0616(8)	0.0943(6)	0.0572(5)	4.7(5)
N(7)	0.0797(9)	0.0766(7)	−0.226(5)	5.1(6)
N(8)	0.1752(9)	0.1316(6)	−0.0677(5)	4.9(6)
C(1)	0.2905(10)	0.3329(7)	0.5668(5)	4.1(6)
C(2)	0.4145(10)	0.2528(8)	0.5779(6)	4.7(6)
C(3)	0.4844(14)	0.1755(10)	0.5205(8)	7(1)
C(4)	0.6034(15)	0.1007(11)	0.5330(11)	9(1)
C(5)	0.6556(15)	0.1021(11)	0.6023(9)	8(1)
C(6)	0.5859(16)	0.1779(12)	0.6594(8)	8(1)
C(7)	0.4637(14)	0.2524(10)	0.6503(7)	6.4(9)
C(8)	0.3965(14)	0.4609(12)	0.3199(9)	8(1)
C(9)	0.3835(15)	0.4031(10)	0.2525(9)	8(1)
C(10)	0.2644(17)	0.4575(12)	0.2238(7)	8(1)
C(11)	0.203(2)	0.5501(11)	0.2683(11)	10(1)
C(12)	0.2809(18)	0.5504(12)	0.3275(11)	8(1)
C(13)	0.526(2)	0.427(2)	0.3591(14)	15(2)
C(14)	0.043(2)	0.2214(12)	0.4141(10)	8(1)
C(15)	0.1524(17)	0.2037(10)	0.3378(15)	9(1)
C(16)	0.089(2)	0.2542(15)	0.2789(8)	9(1)
C(17)	−0.048(2)	0.3018(12)	0.3207(12)	9(1)
C(18)	−0.072(2)	0.2827(15)	0.3991(11)	9(2)
C(19)	0.008(4)	0.194(3)	0.5005(17)	25(5)
C(20)	0.2137(10)	0.1834(7)	−0.0121(5)	4.4(6)
C(21)	0.3181(11)	0.2526(8)	−0.0342(6)	5.0(7)
C(22)	0.3670(14)	0.2919(9)	0.0267(6)	6.5(9)
C(23)	0.4709(18)	0.3547(12)	0.00511(8)	9(1)
C(24)	0.5214(19)	0.3794(12)	−0.0731(9)	9(1)
C(25)	0.476(2)	0.3434(14)	−0.134(8)	10(1)
C(26)	0.3721(14)	0.2784(10)	−0.1146(6)	7(1)
C(27)	−0.4044(14)	0.0819(13)	0.1750(15)	10(1)
C(28)	−0.3791(18)	0.0713(14)	0.2560(11)	9(1)
C(29)	−0.296(2)	0.1365(14)	0.2650(9)	9(1)
C(30)	−0.2619(15)	0.1893(10)	0.1946(11)	8(1)
C(31)	−0.3225(15)	0.1575(12)	0.1350(8)	8(1)
C(32)	−0.498(2)	0.035(2)	0.135(2)	20(3)
C(33)	0.088(3)	−0.1729(15)	0.1787(15)	11(2)
C(34)	−0.029(2)	−0.165(2)	0.2461(16)	12(2)
C(35)	−0.067(4)	−0.070(3)	0.2987(11)	24(4)
C(36)	0.083(4)	−0.0385(16)	0.2498(19)	16(3)
C(37)	0.151(2)	−0.093(2)	0.1831(18)	14(2)

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