Bis($\eta^5$-cyclopentadienyl)(2-[(2-methoxyphenyl)imino]methyl)phenolato-$\kappa^3O,N,O'$terbium

Mikhail E. Minyaev,* Konstantin A. Lyssenko, Dmitrii M. Roitershtein, and Ilya E. Nifant’ev

The air- and moisture-sensitive title compound, [Tb(C$_5$H$_5$)$_2$(C$_{14}$H$_{12}$NO$_2$)], was synthesized from tris(cyclopentadienyl)(tetrahydrofuran)terbium and 2-[(2-methoxyphenyl)imino]methylphenol. Each Tb atom is coordinated by two cyclopentadienyl ligands in an $\eta^5$-coordinated mode and by one N and two O atoms of the organic ligand in a tridentate $\kappa^3O,N,O'$-mode.

1. Chemical context

Bis(cyclopentadienyl) complexes of rare-earth metals attract significant attention because of their important role in the development of organometallic chemistry of 4$f$ elements (Schumann et al., 1995; Wedal & Evans, 2021; Evans, 2016). This type of complex is one of the first discovered organolanthanide classes (Maginn et al., 1963).

The vigorous interest in cyclopentadienyl complexes for the chemistry of rare-earth elements is mainly due to the simplicity of cyclopentadienyl ligand modification by replacing the hydrogen atoms of the five-membered ring with various organic fragments (Harder et al., 2013; Roitershtein, Puntus et al., 2018; Hou & Wakatsuki, 2002). Moreover, in the case of bis(cyclopentadienyl) derivatives such as (C$_5$H$_5$)$_2$LnX, the additional anionic ligand $X^-$ can be coordinated in a mono-, bi- or, as in the present case, a tridentate mode. Such a combination of ligands provides an extremely broad structural diversity for cyclopentadienyl derivatives (Edelmann & Poremba, 1997; Goodwin et al., 2018). This report describes the synthesis and crystal structure of bis($\eta^5$-cyclopentadienyl)(2-[(2-methoxyphenyl)imino]methyl)phenolato)terbium, which is a product of the partial protonation of the tris(cyclopentadienyl)terbium complex with 2-[(2-methoxyphenyl)imino]methylphenol (Fig. 1).
2. Structural commentary

The title compound (Fig. 2) crystallizes in the orthorhombic Pbcn space group (Z' = 1). Assuming that each cyclopentadienyl ligand donates three electron pairs, the terbium atom may be considered to be ennea-coordinated. Both cyclopentadienyl ligands are nearly symmetrically C175-coordinated to the Tb³⁺ cation. Thus, the Cp (centroid)—Tb distances [2.4207 (11) Å for the C1–C5 Cp ring and 2.4062 (10) Å for the C6–C10 Cp ring] are almost equal to the Cp (plane)—Tb distances [2.4196 (11) Å for C1–C5 Cp ring and 2.4054 (10) Å for C6–C10 Cp ring], and the CCp—Tb bond lengths are similar within each ring (Table 1). At the same time, the average CCp—Tb distance to the C1–C5 ring is longer by 0.011 Å than to the second Cp ligand. Such a slight asymmetry is caused by the presence of the tridentate asymmetric 2-[(2-methoxyphenyl)imino]methyl]phenolate (L/C0) ligand. Atoms of the ligand are situated in two planes formed by the following sets of atoms: O1, C11–C16, N1, C24 (r.m.s. deviation = 0.0167 Å) and O2, C17–C23, N1 (r.m.s. deviation = 0.0333 Å). The dihedral angle between these planes of 44.58 (5)° indicates a perceptible loss of conjugation between two parts of the ligand due to the tridentate κ³N,O,O'-coordination mode. The bond redistribution within the ligand (see table in the supporting information) and the Tb—O and Tb—N bond distances (Table 1) are in good agreement with the expected predominant resonance form (see scheme) and with a significant localization of the negative charge on the O2 atom.

It should be noted that analogous compounds with the same L⁻⁻ ligand [(C₅H₅)₂Ln(O₂NC₅H₁₂)] (Ln = Sm, Er, Dy, Y) were previously synthesized in low yields (Yousaf et al., 2000), and the determined crystal structure of the Sm complex is isostructural with that of the title compound.

Non-covalent interactions are negligible in the title compound.

3. Database survey

At first glance, it looks quite puzzling that according to the Cambridge Structural Database (CSD Version 5.42, update of September 2021; Groom et al., 2016), structures of rare-earth metal complexes with the monoanionic phenolate L/C0 ligand and its substituted (L/C0) or protonated (L/H) derivatives have been poorly studied, whereas the structures of complexes bearing their closest analogs – doubly charged 2-[(2-oxidophenyl)imino]methyl]phenolate and its various derivatives – have been studied moderately. This is, likely, due to the higher stability of the latter complexes, which is presumably caused, in short, by a higher degree of the optimization of electrostatic interactions (Evans, 1987). Thus, only 15 complexes bearing L⁻⁻, L⁻⁻, LH and L' ligands have been studied structurally; the corresponding CSD codes are KESHOH (Li & Yuan, 2012), KINHUN, KINJAV, KINJEZ, KINJID, KINJOJ (Roitershtein, Minashina et al., 2018), MIQTAH01 (Yousaf et al., 2000), RAPTUA (Li & Cui, 2017), RUQQEC (Pikoli et al., 2020), VUVMUX, VUVNAE (Long et al., 2020) and the heterometallic Zn/Dy complexes TUQWAG, TUQWEK, TUQWIO, TUQWOU (Shukla et al., 2020). Careful analysis reveals the structural diversity of the coordination modes for L⁻⁻, L⁻⁻, LH and L' ligands in the above-mentioned complexes. Even the sole ligand L⁻⁻ itself can demonstrate different coordination modes in mononuclear rare-earth complexes (Roitershtein, Minashina et al., 2018). Amazingly, only one structure (MIQTAH01) among the 15 corresponds to the organolanthanide bis(cyclopentadienyl) type.

4. Synthesis and crystallization

Synthetic operations were carried out in a glovebox under a purified argon atmosphere. THF was distilled from sodium/
Table 2. Experimental details.

| Crystal data | Chemical formula | [Tb(C₅H₅)₂(C₁₄H₁₂NO₂)] |
|--------------|------------------|--------------------------|
| Mₚ           | 515.34           |                           |
| Crystal system, space group | Orthorhombic, Pbcn |                           |
| Temperature (K) | 120             |                           |
| a, b, c (Å)   | 21.6309 (12), 14.4923 (8), 12.6471 (7) |                           |
| V (Å³)        | 3964.6 (4)       |                           |
| Z             | 8                |                           |
| Radiation type | Mo Kα            |                           |
| μ (mm⁻¹)      | 3.59             |                           |
| Crystal size (mm) | 0.32 × 0.21 × 0.19 |                           |

Data collection

| Diffractometer | Bruker APEXI2 CCD area detector |
|----------------|-------------------------------|
| Absorption correction | Multi-scan (SADABS; Krause et al., 2015) |
| Tmin, Tmax | 0.333, 0.569 |
| No. of observed reflections | 60268, 7485, 5865 |
| R(int) | 0.062 |
| (sin θ/λ)max (Å⁻¹) | 0.766 |

Refinement

| R[F² > 2σ(F²)] | 0.025, 0.060, 1.03 |
| No. of reflections | 7485 |
| No. of parameters | 319 |
| H-atom treatment | Only H-atom coordinates refined |
| Δρmax, Δρmin (e Å⁻³) | 1.14, -0.71 |

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benzophenone ketyl, hexane was distilled from Na/K alloy. Tb(C₅H₅)₃(thf) was obtained according to a literature procedure (Wilkinson & Birmingham, 1954).

A solution of 2-[[2-methoxyphenyl]iminomethyl]phenol (0.230 g, 1.01 mmol) in 5 ml of THF was added slowly to a solution of Tb(C₅H₅)₃(thf) (0.426 g, 1.0 mmol) in 15 ml of THF. The reaction mixture was stirred for 24 h. The solution was concentrated under vacuum to a volume of ca 8–10 ml, and hexane (10 ml) was carefully layered on top of the resulting solution to initiate crystallization. Crystals obtained after several days were dried under vacuum for 1 h, yielding 0.315 g (0.61 mmol, 61%). The terbium content was determined by direct complexometric titration with the disodium salt of EDTA, using xylenol orange indicator (Vogel, 1966). Calculated for C₂₆H₃₃NO₂Tb: Tb, 30.84%. Found Tb, 30.45%.

Single crystals suitable for X-ray diffraction study were taken from a vial with a crude product before drying under vacuum.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The structure was in general solved by dual methods (SHELXT; Sheldrick, 2015a). Positions of remaining non-H atoms were found from the difference electron density maps. All non-H atoms were refined anisotropically. The positions of hydrogen atoms were refined with Uiso(H) = 1.5Ueq(C) for methyl group and Uiso(H) = 1.2Ueq(C) for others.

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Computing details

Data collection: APEX2 (Bruker, 2016); cell refinement: SAINT (Bruker, 2016); data reduction: SAINT (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: SHELXL2018 (Sheldrick, 2015b); molecular graphics: Mercury (Macrae et al., 2020); software used to prepare material for publication: publCIF (Westrip, 2010).

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Crystal data

[Tb(C₅H₅)₂(C₁₄H₁₂NO₂)]
Mr = 515.34
Orthorhombic, Pbcn
a = 21.6309 (12) Å
b = 14.4923 (8) Å
c = 12.6471 (7) Å
V = 3964.6 (4) Å³
Z = 8
F(000) = 2032

Data collection

Bruker APEXII CCD area detector diffractometer
Radiation source: sealed X-ray tube
Graphite monochromator
Detector resolution: 7.31 pixels mm⁻¹
ω scans
Absorption correction: multi-scan
(SADABS; Krause et al., 2015)
Tmin = 0.333, Tmax = 0.569

Refinement

Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.025
wR(F²) = 0.060
S = 1.03
7485 reflections
319 parameters
0 restraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
Only H-atom coordinates refined

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Supporting information

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating $R$-factors(gt) etc. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)

|     | x       | y       | z       | $U_{iso}$/$U_{eq}$ |
|-----|---------|---------|---------|-------------------|
| Tb  | 0.65689 (2) | 0.77625 (2) | 0.32099 (2) | 0.01273 (3) |
| O1  | 0.61771 (7) | 0.82735 (11) | 0.50164 (12) | 0.0193 (3) |
| O2  | 0.63302 (8) | 0.67000 (11) | 0.20325 (12) | 0.0190 (3) |
| N1  | 0.56840 (8) | 0.68915 (12) | 0.39465 (14) | 0.0144 (3) |
| C1  | 0.74352 (13) | 0.7329 (2) | 0.4689 (2) | 0.0378 (7) |
| H1  | 0.7343 (16) | 0.741 (2) | 0.539 (3) | 0.045* |
| C2  | 0.77065 (12) | 0.7984 (2) | 0.4006 (2) | 0.0328 (6) |
| H2  | 0.7832 (15) | 0.859 (2) | 0.415 (3) | 0.039* |
| C3  | 0.77899 (11) | 0.75538 (19) | 0.3010 (2) | 0.0259 (5) |
| H3  | 0.7968 (14) | 0.786 (2) | 0.242 (3) | 0.031* |
| C4  | 0.75698 (12) | 0.66501 (19) | 0.3091 (2) | 0.0263 (5) |
| H4  | 0.7546 (14) | 0.620 (2) | 0.256 (2) | 0.032* |
| C5  | 0.73448 (13) | 0.6512 (2) | 0.4122 (2) | 0.0337 (6) |
| C6  | 0.65210 (11) | 0.96160 (15) | 0.3007 (2) | 0.0225 (5) |
| C7  | 0.68593 (11) | 0.92900 (15) | 0.2132 (2) | 0.0223 (5) |
| C8  | 0.64535 (11) | 0.87859 (16) | 0.1473 (2) | 0.0209 (4) |
| C9  | 0.6550 (12) | 0.851 (2) | 0.083 (2) | 0.025* |
| C10 | 0.58601 (11) | 0.88127 (15) | 0.19414 (19) | 0.0201 (4) |
| C11 | 0.5550 (14) | 0.850 (2) | 0.168 (2) | 0.024* |
| C12 | 0.59022 (11) | 0.93258 (15) | 0.2884 (2) | 0.0208 (4) |
| C13 | 0.5550 (14) | 0.943 (2) | 0.334 (2) | 0.025* |
| C14 | 0.55636 (10) | 0.80986 (14) | 0.52484 (17) | 0.0157 (4) |
| C15 | 0.53032 (10) | 0.73486 (13) | 0.47039 (16) | 0.0141 (4) |
| C16 | 0.46845 (10) | 0.71343 (15) | 0.48786 (17) | 0.0180 (4) |
| C17 | 0.4491 (12) | 0.6662 (19) | 0.448 (2) | 0.022* |
| C18 | 0.43354 (11) | 0.76366 (17) | 0.55984 (19) | 0.0224 (5) |
| C19 | 0.3905 (14) | 0.750 (2) | 0.569 (2) | 0.027* |
| C20 | 0.46002 (11) | 0.83688 (17) | 0.61333 (19) | 0.0227 (5) |
| C21 | 0.4365 (14) | 0.875 (2) | 0.657 (2) | 0.027* |
| C22 | 0.52167 (11) | 0.86056 (16) | 0.59584 (18) | 0.0209 (4) |
| C23 | 0.5394 (13) | 0.907 (2) | 0.632 (2) | 0.025* |

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### Atomic displacement parameters (Å²)

|   | \(U^{11}\)    | \(U^{22}\)    | \(U^{33}\)    | \(U^{12}\)    | \(U^{13}\)    | \(U^{23}\)    |
|---|----------------|----------------|----------------|----------------|----------------|----------------|
| Tb1 | 0.0116 (5)   | 0.0106 (4)   | 0.0159 (5)   | 0.00074 (3)  | −0.00014 (3)  | 0.00054 (3)  |
| O1  | 0.0168 (7)   | 0.0194 (7)   | 0.0216 (8)   | −0.0033 (6)  | 0.0009 (6)   | −0.0079 (6)  |
| O2  | 0.0274 (8)   | 0.0121 (6)   | 0.0176 (7)   | −0.0002 (6)  | 0.0015 (6)   | 0.0001 (6)   |
| N1  | 0.0164 (8)   | 0.0135 (8)   | 0.0135 (8)   | 0.0009 (6)   | −0.0009 (6)  | −0.0010 (6)  |
| C1  | 0.0269 (13)  | 0.065 (2)    | 0.0213 (12)  | 0.0232 (14)  | −0.0049 (10) | 0.0018 (13)  |
| C2  | 0.0179 (11)  | 0.0381 (15)  | 0.0423 (16)  | 0.0055 (10)  | −0.0116 (11) | −0.0095 (12) |
| C3  | 0.0139 (10)  | 0.0319 (12)  | 0.0319 (14)  | 0.0049 (9)   | 0.0009 (9)   | 0.0066 (10)  |
| C4  | 0.0198 (11)  | 0.0269 (12)  | 0.0320 (13)  | 0.0116 (9)   | 0.0036 (10)  | 0.0012 (10)  |
| C5  | 0.0260 (13)  | 0.0354 (15)  | 0.0397 (15)  | 0.0159 (11)  | 0.0072 (11)  | 0.0163 (12)  |
| C6  | 0.0237 (11)  | 0.0112 (9)   | 0.0325 (13)  | −0.0014 (8)  | −0.0047 (9)  | −0.0005 (8)  |
| C7  | 0.0174 (10)  | 0.0147 (9)   | 0.0346 (13)  | −0.0013 (8)  | 0.0004 (9)   | 0.0095 (9)   |
| C8  | 0.0255 (12)  | 0.0155 (10)  | 0.0216 (10)  | 0.0045 (8)   | 0.0013 (9)   | 0.0045 (8)   |
| C9  | 0.0192 (10)  | 0.0136 (9)   | 0.0273 (12)  | 0.0011 (8)   | −0.0046 (9)  | 0.0015 (8)   |
| C10 | 0.0203 (11)  | 0.0142 (9)   | 0.0280 (11)  | 0.0036 (8)   | 0.0018 (9)   | 0.0000 (8)   |
| C11 | 0.0167 (9)   | 0.0151 (9)   | 0.0153 (9)   | 0.0001 (7)   | −0.0011 (7)  | −0.0015 (7)  |
| C12 | 0.0162 (9)   | 0.0141 (9)   | 0.0119 (8)   | 0.0002 (7)   | 0.0006 (7)   | 0.0016 (7)   |
| C13 | 0.0161 (9)   | 0.0200 (10)  | 0.0179 (10)  | −0.0028 (8)  | −0.0008 (8)  | 0.0028 (8)   |
| C14 | 0.0176 (10)  | 0.0267 (12)  | 0.0229 (11)  | 0.0015 (9)   | 0.0031 (8)   | 0.0054 (9)   |
| C15 | 0.0248 (12)  | 0.0221 (11)  | 0.0213 (11)  | 0.0041 (9)   | 0.0067 (9)   | −0.0007 (9)  |
| C16 | 0.0258 (12)  | 0.0193 (10)  | 0.0175 (10)  | 0.0017 (9)   | 0.0010 (9)   | −0.0039 (8)  |
| C17 | 0.0182 (10)  | 0.0154 (9)   | 0.0160 (9)   | −0.0015 (8)  | 0.0002 (8)   | −0.0006 (7)  |
| C18 | 0.0189 (10)  | 0.0131 (9)   | 0.0155 (9)   | 0.0000 (7)   | −0.0015 (7)  | −0.0006 (7)  |
| C19 | 0.0191 (10)  | 0.0127 (9)   | 0.0153 (9)   | 0.0014 (7)   | −0.0027 (8)  | −0.0003 (7)  |
| C20 | 0.0265 (11)  | 0.0183 (10)  | 0.0165 (10)  | 0.0033 (9)   | 0.0004 (9)   | −0.0024 (8)  |
| C21 | 0.0260 (12)  | 0.0173 (10)  | 0.0230 (11)  | 0.0048 (9)   | −0.0029 (9)  | −0.0071 (9)  |
| C22 | 0.0285 (12)  | 0.0136 (10)  | 0.0286 (12)  | −0.0002 (9)  | −0.0041 (10) | −0.0042 (9)  |
| C23 | 0.0265 (12)  | 0.0136 (9)   | 0.0237 (11)  | −0.0020 (8)  | 0.0012 (9)   | −0.0005 (8)  |
| C24 | 0.0270 (13)  | 0.0335 (14)  | 0.0324 (14)  | −0.0105 (11) | 0.0005 (11)  | −0.0180 (11) |
### Geometric parameters (Å, °)

| Bond/Distance   | Value   | Bond/Distance   | Value   |
|-----------------|---------|-----------------|---------|
| Tb1—C1          | 2.721 (3) | C7—H7           | 0.91 (3) |
| Tb1—C2          | 2.678 (3) | C8—C9           | 1.414 (3) |
| Tb1—C3          | 2.670 (2) | C8—H8           | 0.93 (3)  |
| Tb1—C4          | 2.704 (2) | C9—C10          | 1.408 (3) |
| Tb1—C5          | 2.726 (3) | C9—H9           | 0.96 (3)  |
| Tb1—C6          | 2.700 (2) | C10—H10         | 0.91 (3)  |
| Tb1—C7          | 2.675 (2) | C11—C16         | 1.382 (3) |
| Tb1—C8          | 2.662 (2) | C11—C12         | 1.405 (3) |
| Tb1—C9          | 2.691 (2) | C12—C13         | 1.392 (3) |
| Tb1—C10         | 2.717 (2) | C13—C14         | 1.389 (3) |
| Tb1—O1          | 2.5468 (15) | Tb1—C2—H2     | 117 (2)  |
| Tb1—O2          | 2.5646 (15) | Tb1—C3—H3     | 122.9 (19) |
| Tb1—N1          | 2.4748 (18) | Tb1—C4—C5     | 108.6 (3) |
| O1—C11          | 1.383 (3) | C15—C16         | 1.395 (3) |
| O1—C24          | 1.451 (3) | C15—H15         | 0.95 (3)  |
| O2—C19          | 1.303 (3) | C16—H16         | 0.90 (3)  |
| N1—C17          | 1.301 (3) | C17—C18         | 1.435 (3) |
| N1—C12          | 1.427 (3) | C17—H17         | 0.95 (3)  |
| C1—C5           | 1.398 (5) | C18—C23         | 1.412 (3) |
| C1—C2           | 1.411 (5) | C18—C19         | 1.424 (3) |
| C1—H1           | 0.91 (4)  | C19—C20         | 1.414 (3) |
| C2—C3           | 1.417 (4) | C20—C21         | 1.380 (3) |
| C2—H2           | 0.94 (3)  | C20—H20         | 0.95 (3)  |
| C3—C4           | 1.397 (4) | C21—C22         | 1.392 (4) |
| C3—H3           | 0.94 (3)  | C21—H21         | 0.91 (3)  |
| C4—C5           | 1.406 (4) | C22—C23         | 1.375 (3) |
| C4—H4           | 0.93 (3)  | C22—H22         | 0.90 (3)  |
| C5—H5           | 0.95 (3)  | C23—H23         | 0.92 (3)  |
| C6—C7           | 1.408 (4) | C24—H24A        | 0.98 (4)  |
| C6—C10          | 1.412 (3) | C24—H24B        | 0.94 (4)  |
| C6—H6           | 0.92 (3)  | C24—H24C        | 0.98 (4)  |
| C7—C8           | 1.413 (4) | C3—C2—H2       | 123 (2)   |
| O2—Tb1—N1       | 73.54 (6) | C3—C2—H2       | 123 (2)   |
| O2—Tb1—O1       | 137.01 (6) | C4—C3—C2      | 107.7 (2) |
| N1—Tb1—O1       | 63.47 (5) | C4—C3—C2      | 107.7 (2) |
| O2—Tb1—C8       | 79.04 (7) | C4—C3—Tb1      | 76.25 (14) |
| N1—Tb1—C8       | 121.49 (7) | C2—C3—Tb1     | 74.94 (14) |
| O1—Tb1—C8       | 123.16 (6) | C4—C3—H3      | 129.4 (19) |
| O2—Tb1—C3       | 95.09 (8)  | C2—C3—H3      | 122.9 (19) |
| N1—Tb1—C3       | 137.96 (7) | Tb1—C3—H3     | 115.1 (19) |
| O1—Tb1—C3       | 116.54 (7) | C3—C4—C5      | 108.6 (3)  |
| C8—Tb1—C3       | 94.46 (8)  | C3—C4—Tb1     | 73.62 (14) |
| O2—Tb1—C7       | 106.80 (7) | C5—C4—Tb1     | 75.87 (14) |
| N1—Tb1—C7       | 142.72 (7) | C3—C4—H4      | 128.1 (19) |
| O1—Tb1—C7       | 107.14 (7) | C5—C4—H4      | 123.2 (19) |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|-----------------------|--------------|-----------------------|--------------|
| C8—Tb1—C7            | 30.72 (8)    | Tb1—C4—H4            | 114.2 (19)   |
| C3—Tb1—C7            | 79.24 (8)    | C1—C5—C4             | 107.9 (3)    |
| O2—Tb1—C2            | 123.58 (8)   | C1—C5—Tb1            | 74.94 (15)   |
| N1—Tb1—C2            | 129.07 (8)   | C4—C5—Tb1            | 74.11 (14)   |
| O1—Tb1—C2            | 86.20 (8)    | C1—C5—H5             | 131 (2)      |
| C8—Tb1—C2            | 109.23 (9)   | C4—C5—H5             | 121 (2)      |
| C3—Tb1—C2            | 30.71 (9)    | Tb1—C5—H5            | 116 (2)      |
| C7—Tb1—C2            | 82.91 (9)    | C7—C6—C10            | 107.9 (2)    |
| O2—Tb1—C9            | 81.89 (6)    | C7—C6—Tb1            | 73.80 (13)   |
| N1—Tb1—C9            | 94.15 (6)    | C10—C6—Tb1           | 75.54 (13)   |
| O1—Tb1—C9            | 100.42 (6)   | C7—C6—H6             | 124.0 (18)   |
| C8—Tb1—C9            | 30.63 (7)    | C10—C6—H6            | 128.1 (18)   |
| C3—Tb1—C9            | 124.84 (8)   | Tb1—C6—H6            | 117.5 (19)   |
| C7—Tb1—C9            | 50.34 (7)    | C6—C7—C8             | 108.3 (2)    |
| C2—Tb1—C9            | 132.83 (9)   | C6—C7—Tb1            | 75.84 (13)   |
| O2—Tb1—C6            | 128.45 (7)   | C8—C7—Tb1            | 74.15 (13)   |
| N1—Tb1—C6            | 120.91 (7)   | C6—C7—H7             | 123.9 (18)   |
| O1—Tb1—C6            | 77.49 (7)    | C8—C7—H7             | 127.8 (18)   |
| C8—Tb1—C6            | 50.48 (8)    | Tb1—C7—H7            | 117.4 (19)   |
| C3—Tb1—C6            | 98.14 (8)    | C7—C8—C9             | 107.6 (2)    |
| C7—Tb1—C6            | 30.36 (8)    | C7—C8—Tb1            | 75.14 (13)   |
| C2—Tb1—C6            | 87.23 (8)    | C9—C8—Tb1            | 75.82 (13)   |
| C9—Tb1—C6            | 50.12 (7)    | C7—C8—H8             | 126.8 (17)   |
| O2—Tb1—C4            | 74.52 (7)    | C9—C8—H8             | 125.6 (17)   |
| N1—Tb1—C4            | 109.64 (7)   | Tb1—C8—H8            | 117.0 (18)   |
| O1—Tb1—C4            | 119.34 (7)   | C10—C9—C8            | 108.1 (2)    |
| C8—Tb1—C4            | 111.18 (8)   | C10—C9—Tb1           | 75.93 (13)   |
| C3—Tb1—C4            | 30.13 (8)    | C8—C9—Tb1            | 73.55 (13)   |
| C7—Tb1—C4            | 106.08 (8)   | C10—C9—H9            | 126.6 (17)   |
| C2—Tb1—C4            | 49.96 (9)    | C8—C9—H9             | 125.3 (17)   |
| C9—Tb1—C4            | 139.49 (8)   | Tb1—C9—H9            | 113.8 (17)   |
| C6—Tb1—C4            | 128.21 (8)   | C9—C10—C6            | 108.1 (2)    |
| O2—Tb1—C10           | 110.85 (7)   | C9—C10—Tb1           | 73.89 (13)   |
| N1—Tb1—C10           | 94.13 (7)    | C6—C10—Tb1           | 74.25 (13)   |
| O1—Tb1—C10           | 73.55 (6)    | C9—C10—H10           | 124.7 (18)   |
| C8—Tb1—C10           | 50.25 (7)    | C6—C10—H10           | 127.2 (18)   |
| C3—Tb1—C10           | 127.23 (8)   | Tb1—C10—H10          | 116.7 (18)   |
| C7—Tb1—C10           | 50.00 (7)    | C16—C11—O1           | 124.17 (19)  |
| C2—Tb1—C10           | 116.40 (8)   | C16—C11—C12          | 120.8 (2)    |
| C9—Tb1—C10           | 30.19 (7)    | O1—C11—C12           | 115.01 (18)  |
| C6—Tb1—C10           | 30.20 (7)    | C13—C12—C11          | 118.72 (19)  |
| C4—Tb1—C10           | 156.04 (8)   | C13—C12—N1           | 123.94 (19)  |
| O2—Tb1—C1            | 117.67 (8)   | C11—C12—N1           | 117.20 (19)  |
| N1—Tb1—C1            | 98.95 (8)    | C14—C13—C12          | 120.7 (2)    |
| O1—Tb1—C1            | 71.32 (7)    | C14—C13—H13          | 119.3 (16)   |
| C8—Tb1—C1            | 139.49 (9)   | C12—C13—H13          | 120.0 (16)   |
| C3—Tb1—C1            | 50.03 (9)    | C15—C14—C13          | 119.8 (2)    |
| C7—Tb1—C1            | 112.31 (9)   | C15—C14—H14          | 120.3 (18)   |
| Bond Symbol | Distance (Å) | Bond Symbol | Distance (Å) |
|-------------|-------------|-------------|-------------|
| C2—Tb1—C1  | 30.29 (10)  | C13—C14—H14 | 119.8 (18)  |
| C9—Tb1—C1  | 158.87 (9)  | C14—C15—C16 | 120.5 (2)   |
| C6—Tb1—C1  | 108.76 (9)  | C14—C15—H15 | 120.2 (19)  |
| C4—Tb1—C1  | 49.39 (9)   | C16—C15—H15 | 119.0 (19)  |
| C10—Tb1—C1 | 131.47 (9)  | C11—C16—C15 | 119.4 (2)   |
| O2—Tb1—C5  | 88.02 (8)   | C11—C16—H16 | 119.8 (19)  |
| N1—Tb1—C5  | 88.73 (7)   | C15—C16—H16 | 120.8 (18)  |
| O1—Tb1—C5  | 91.07 (7)   | N1—C17—C18  | 127.2 (2)   |
| C8—Tb1—C5  | 141.00 (8)  | N1—C17—H17  | 118.6 (16)  |
| C3—Tb1—C5  | 49.89 (8)   | C18—C17—H17 | 114.2 (16)  |
| C7—Tb1—C5  | 128.41 (8)  | C23—C18—C19 | 119.6 (2)   |
| C2—Tb1—C5  | 49.83 (10)  | C23—C18—C17 | 117.3 (2)   |
| C9—Tb1—C5  | 168.24 (8)  | C19—C18—C17 | 122.92 (19) |
| C6—Tb1—C5  | 136.49 (9)  | O2—C19—C20  | 120.5 (2)   |
| C4—Tb1—C5  | 30.02 (8)   | O2—C19—C18  | 122.27 (19) |
| C10—Tb1—C5 | 160.96 (9)  | C20—C19—C18 | 117.18 (19) |
| C1—Tb1—C5  | 29.74 (10)  | C21—C20—C19 | 121.6 (2)   |
| C11—O1—C24 | 115.77 (18) | C21—C20—H20 | 122.1 (19)  |
| C11—O1—Tb1 | 117.16 (12) | C19—C20—H20 | 116.3 (19)  |
| C11—O1—Tb1 | 117.16 (12) | C20—C21—C22 | 121.1 (2)   |
| C24—O1—Tb1 | 122.42 (15) | C20—C21—H21 | 117.7 (19)  |
| C19—O2—Tb1 | 133.53 (14) | C22—C21—H21 | 121.1 (19)  |
| C17—N1—C12 | 117.59 (18) | C22—C21—H21 | 118.8 (2)   |
| C17—N1—Tb1 | 124.56 (15) | C23—C22—C21 | 120.3 (19)  |
| C12—N1—Tb1 | 117.54 (12) | C23—C22—C21 | 120.9 (19)  |
| C5—C1—C2   | 108.3 (3)   | C21—C22—C23 | 121.8 (2)   |
| C5—C1—C2   | 108.3 (3)   | C22—C23—C18 | 123.1 (18)  |
| C2—C1—Tb1  | 73.17 (15)  | C22—C23—C18 | 115.1 (18)  |
| C5—C1—H1   | 125 (2)     | C18—C23—H23 | 105 (2)     |
| C2—C1—H1   | 127 (2)     | O1—C24—H24A | 111 (2)     |
| Tb1—C1—C2  | 119 (2)     | O1—C24—H24B | 113 (3)     |
| C1—C2—C3   | 107.5 (3)   | H24A—C24—H24B | 113 (3) |
| C1—C2—Tb1  | 76.54 (16)  | O1—C24—H24C | 110 (3)     |
| C3—C2—Tb1  | 74.34 (14)  | H24A—C24—H24C | 110 (3) |
| C1—C2—H2   | 129 (2)     | C24—H24A—C24—H24C | 110 (3) |

| Bond Symbol | Angle (°) | Bond Symbol | Angle (°) |
|-------------|----------|-------------|----------|
| C5—C1—C2  | 67.73 (19)| C16—C11—C12—C13 | −178.98 (18) |
| C5—C1—C2  | 67.73 (19)| C16—C11—C12—N1 | 176.94 (19) |
| C1—C2—C3  | 0.2 (3)  | O1—C11—C12—N1 | −3.2 (3) |
| Tb1—C2—C3 | −69.85 (18)| C17—N1—C12—C13 | −32.4 (3) |
| C1—C2—C3  | 70.01 (18)| C17—N1—C12—C13 | 153.66 (16) |
| C2—C3—C4  | 0.5 (3)  | Tb1—N1—C12—C13 | 153.66 (16) |
| Tb1—C3—C4 | −68.45 (18)| C17—N1—C12—C13 | 152.0 (2) |
| C2—C3—C4  | 68.95 (17)| Tb1—N1—C12—C13 | −21.9 (2) |
| C2—C1—C5  | 1.1 (3)  | C11—C12—C13—C14 | −1.7 (3) |
| Tb1—C1—C5 | 67.38 (18)| N1—C12—C13—C14 | −177.2 (2) |
| C2—C1—C5  | −66.30 (19)| C12—C13—C14—C15 | 1.3 (3) |
| C3—C4—C5  | −1.0 (3) | C13—C14—C15—C16 | −0.2 (4) |
| Bond                  | Angle (°)        | Bond                  | Angle (°)        |
|----------------------|------------------|----------------------|------------------|
| Tb1—C4—C5—C1        | −67.94 (19)      | O1—C11—C16—C15      | 180.0 (2)        |
| C3—C4—C5—Tb1        | 66.96 (18)       | C12—C11—C16—C15     | −0.1 (3)         |
| C10—C6—C7—C8        | −0.8 (3)         | C14—C15—C16—C11     | −0.3 (4)         |
| Tb1—C6—C7—C8        | 67.66 (16)       | C12—N1—C17—C18      | 171.9 (2)        |
| C10—C6—C7—Tb1       | −68.48 (16)      | Tb1—N1—C17—C18      | −14.6 (3)        |
| C6—C7—C8—C9         | 0.7 (3)          | N1—C17—C18—C23      | 173.7 (2)        |
| Tb1—C7—C8—C9        | 69.50 (16)       | N1—C17—C18—C19      | −12.3 (4)        |
| C6—C7—C8—Tb1        | −68.79 (16)      | Tb1—O2—C19—C20      | −146.18 (18)     |
| C7—C8—C9—C10        | −0.3 (3)         | Tb1—O2—C19—C18      | 36.0 (3)         |
| Tb1—C8—C9—C10       | 68.71 (16)       | C23—C18—C19—O2      | 179.2 (2)        |
| C7—C8—C9—Tb1        | −69.03 (16)      | C17—C18—C19—O2      | 5.2 (3)          |
| C8—C9—C10—C6        | −0.2 (3)         | C23—C18—C19—C20     | 1.3 (3)          |
| Tb1—C9—C10—C6       | 66.92 (16)       | C17—C18—C19—C20     | −172.6 (2)       |
| C8—C9—C10—Tb1       | −67.12 (16)      | O2—C19—C20—C21      | −179.6 (2)       |
| C7—C6—C10—C9        | 0.6 (3)          | C18—C19—C20—C21     | −1.6 (3)         |
| Tb1—C6—C10—C9       | −66.68 (16)      | C19—C20—C21—C22     | 0.7 (4)          |
| C7—C6—C10—Tb1       | 67.31 (16)       | C20—C21—C22—C23     | 0.7 (4)          |
| C24—O1—C11—C16      | 2.4 (3)          | C21—C22—C23—C18     | −1.1 (4)         |
| Tb1—O1—C11—C16      | −154.05 (18)     | C19—C18—C23—C22     | 0.1 (4)          |
| C24—O1—C11—C12      | −177.5 (2)       | C17—C18—C23—C22     | 174.3 (2)        |