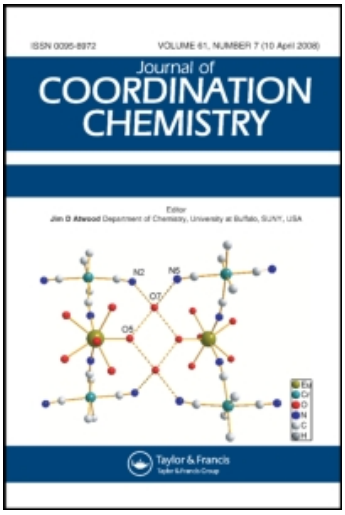

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SYNTHESIS AND STRUCTURE OF DINUCLEAR COMPLEXES OF TERBIUM(III) WITH 4-ACETALBISPYRAZOLONE

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SYNTHESIS AND STRUCTURE OF DINUCLEAR COMPLEXES OF TERBIUM(III) WITH 4-ACETALBISPYRAZOLONE

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Two novel dinuclear complexes of terbium(III) with 1,5-bis(1'-phenyl-3'-methyl-5'-pyrazolone-4')-1,5-pentanedione (H_2L), $Tb_2L_3 \cdot 6H_2$), $Tb_2L_3 \cdot 5DMF$, have been synthesized. The crystal structure of $Tb_2L_3 \cdot 5DMF$ was determined by X-ray diffraction methods. Crystals are triclinic, space group $P\bar{1}$ with a = 16.957(5), b = 17.877(7), c = 18.269(2)Å, α = 110.35(2), β = 101.29(2), γ = 111.00(2)°, V = 4511(6)Å^3, Mr = 2010.76, Z = 2, Dx = 1.48 g cm^{-3}, μ = 16.45 cm^{-1}, $F(000)$ = 2,052, R = 0.058 with 6574 reflections used in refinement. In the complex, L acts as a bridging ligand and bonds two terbium atoms with its two β-diketone groups. Each terbium ion bonds to two DMF solvent molecules. The coordination number of the two terbium ions is eight. The eight oxygen atoms around the terbium make a distorted square antiprismatic coordination polyhedron.

KEYWORDS: pyrazolone, tetraketone, dinuclear complex, terbium, X-ray structure

INTRODUCTION

4-Acetylbispyrazolones represent a new type of chelating ligand which has two constituent β-diketones. They are more efficient than 1-phenyl-3-methyl-5-pyrazolone derivatives in extracting 'hard' Lewis acid metal ions such as rare earth ions.[1] Bispyrazolone rare earth complexes show strong fluorescence[2–4] and some possess antitumor activity *in vitro* and high herbicidal activity[5]. However, metal complexes containing bispyrazolone which are structurally characterized have not been reported, to our knowledge. Recently we were successful in the synthesis and structural characterization of complexes of rare earths with the title polydentate ligands. In this paper, we report the molecular and crystal structure of the dinuclear complex of 1,5-bis(1'-phenyl-3'-methyl-5'-pyrazolone-4')-1,5-pentanedione (H_2L)[6] with terbium(III) ion.

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EXPERIMENTAL

Synthesis of $Tb_2L_3 \cdot 6H_2O$

Aqueous 2 mmol NaOH was added slowly to an ethanol solution containing 1 mmol of H_2L, with stirring. Then, 2 mmol of Tb $(NO_3)_3$ in water was added slowly to the above solution with stirring at room temperature. The mixture was continually stirred for about ten hours. A white precipitate was obtained. The product was collected and washed throughly with ethanol, water and ethanol respectively, then dried in air at room temperature. Yeild: >85%. Anal.: calc. for $Tb_2L_3 \cdot 6H_2O$: C, 51.4; H, 4.5; N, 9.6%. Found: C, 51.2; H, 4.4; N, 9.2%.

Synthesis of $Tb_2L_3 \cdot 5DMF$

A little $Tb_2L_3 \cdot 6H_2O$ was dissolved in *N,N*-dimethylformamide. The dilute solution was evaporated very slowly at room temperature for several months, when single crystals suitable for X-ray data collection were obtained.

X-ray data collection, structure determination and refinement for complex $Tb_2L_3 \cdot 5DMF$

A transparent colourless crystal having approximate dimensions 0.2 × 0.3 × 0.3 mm was mounted on a glass fibre in random orientation. The determination of the unit cell and data collection was performed with Mo-Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal monochromator. A total of 10023 independent reflections were collected in the range $2° \leqslant \theta \leqslant 21°$ by the ω–2θ scan technique at room temperature (23 ± 1 °C) of which 6574 reflections with $I \geq 3\sigma(I)$ were considered to be observed and used in the subsequent refinement. Correction for Lp effects was applied to the data.

Crystals are triclinic, space group $P\bar{1}$, with a = 16.957(5), b = 17.877(7), c = 18.269(2)Å, α = 110.35(2), β = 101.29(2), γ = 111.00(2)°, V = 4511(6)Å^3, Mr = 2010.76, Z = 2, Dx = 1.48 g/cm^3, μ = 16.45 cm^{-1}, $F(000)$ = 2052.

The structure was solved by direct methods (MULTAN 82). The positions of the two terbium atoms were located on an E-map. All other non-hydrogen atoms were determined from successive difference Fourier syntheses.

The final refinement by full-matrix least-squares with isotropic thermal parameters for all of the carbon atoms and anisotropic thermal parameters for other non-hydrogen atoms converged with agreement factors of $R = \Sigma|\Delta F|/\Sigma|F_o| = 0.058$ and $R_w = [\Sigma w|\Delta F|^2/\Sigma|F_o|^2]^{1/2} = 0.067$ (unit weights for all observed reflections). The largest peak in the final difference Fourier map had a height of 0.80 eÅ^{-3}. All calculations were performed on a PDP 11/44 computer using the SDP-PLUS program system.

RESULTS AND DISCUSSION

The molecular structure of the complex $Tb_2L_3 \cdot 5DMF$ is shown in Figure 1. Fractional coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Table 1. Significant bond lengths and angles are given

Table 1 Fractional coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms

Atom	*x/a*	y/b	z/c	Beq(Å^2)
Tb(1)	0.17135(4)	0.31153(4)	0.17511(4)	3.27(2)
Tb(2)	0.41178(5)	0.18722(4)	-0.15084(4)	3.13(2)
O(1)	0.3765(7)	0.0456(6)	-0.1639(6)	4.7(3)
O(2)	0.4041(6)	0.1921(6)	-0.0189(6)	4.7(3)
O(3)	0.3162(6)	0.3213(5)	0.20007(5)	3.8(3)
O(4)	0.2400(6)	0.3738(5)	0.3185(5)	3.9(2)
O(5)	0.3334(6)	0.0944(6)	-0.2923(5)	4.0(3)
O(6)	0.2553(7)	0.1336(6)	-0.1745(6)	4.8(3)
O(7)	0.1332(7)	0.1884(5)	0.0468(6)	4.8(3)
O(8)	0.1520(6)	0.1892(6)	0.2019(6)	4.8(3)
O(9)	0.5539(5)	0.2893(5)	-0.0533(5)	3.3(2)
O(10)	0.3987(6)	0.3184(5)	-0.0800(5)	3.7(3)
O(11)	0.2384(6)	0.3903(5)	0.1040(6)	4.4(3)
O(12)	0.1783(6)	0.4517(5)	0.2353(5)	4.2(3)
N(1)	0.3646(8)	-0.0716(7)	-0.1302(7)	4.8(4)
N(2)	0.3717(9)	-0.0837(7)	-0.0591(8)	5.4(4)
N(3)	0.3241(7)	0.3909(7)	0.4442(6)	3.7(3)
N(4)	0.4030(8)	0.3860(8)	0.4786(7)	4.6(4)
N(5)	0.2237(8)	-0.0405(7)	-0.4099(7)	4.3(4)
N(6)	0.1316(9)	-0.1029(9)	-0.4379(8)	5.7(4)
N(7)	0.1615(8)	0.0613(7)	0.1939(7)	4.3(3)
N(8)	0.1583(9)	-0.0145(7)	0.1325(8)	5.5(4)
(N9)	0.6523(7)	0.3937(6)	0.0839(6)	3.4(3)
N(10)	0.6592(8)	0.4662(7)	0.1536(7)	4.1(3)
N(11)	0.1712(7)	0.5798(7)	0.2433(7)	3.8(3)
N(12)	0.1844(8)	0.6309(6)	0.2006(7)	4.3(3)
C(11)	0.3492(9)	-0.1391(9)	-0.2059(9)	4.3(3)*
C(12)	0.319(1)	-0.1377(9)	-0.282(1)	4.9(4)*
C(13)	0.303(1)	-0.210(1)	-0.358(1)	5.7(4)*
C(14)	0.319(1)	-0.281(1)	-0.352(1)	5.7(4)*
C(15)	0.343(1)	-0.284(1)	-0.279(1)	6.0(4)*
C(16)	0.364(1)	-0.212(1)	-0.201(1)	5.5(4)*
C(17)	0.3753(9)	0.0166(9)	-0.1096(9)	4.1(3)*
C(18)	0.3884(9)	0.0563(8)	-0.0237(8)	3.7(3)*
C(19)	0.385(1)	-0.0101(9)	0.004(1)	4.9(4)*
C(20)	0.396(1)	-0.006(1)	0.088(1)	5.8(4)*
C(21)	0.3979(9)	0.1434(9)	0.0146(9)	4.2(3)*
C(22)	0.400(1)	0.1919(9)	0.1051(9)	4.7(4)*
C(23)	0.4491(9)	0.2852(9)	0.1506(9)	4.1(3)*
C(24)	0.4608(9)	0.3216(9)	0.2436(9)	4.3(4)*
C(25)	0.3777(9)	0.3303(8)	0.2588(8)	3.5(3)*
C(31)	0.2758(9)	0.4108(8)	0.4962(8)	3.6(3)*
C(32)	0.192(1)	0.404(1)	0.462(1)	7.2(5)*
C(33)	0.145(1)	0.425(1)	0.517(1)	9.2(7)*
C(34)	0.184(1)	0.456(1)	0.602(1)	6.1(4)*
C(35)	0.267(1)	0.465(1)	0.634(1)	5.8(4)*
C(36)	0.316(1)	0.4415(9)	0.5815(9)	4.9(4)*
C(37)	0.3063(9)	0.3727(8)	0.3622(8)	3.4(3)*
C(38)	0.3753(8)	0.3537(8)	0.3414(8)	3.1(3)*
C(39)	0.4326(9)	0.3656(9)	0.4171(9)	4.2(3)*
C(40)	0.517(1)	0.354(1)	0.434(1)	5.9(4)*
C(41)	0.2729(9)	-0.0527(9)	-0.4628(9)	4.1(3)*
C(42)	0.234(1)	-0.139(1)	-0.534(1)	5.2(4)*
C(43)	0.284(1)	-0.152(1)	-0.586(1)	5.4(4)*
C(44)	0.363(1)	-0.085(1)	-0.573(1)	6.2(5)*
C(45)	0.400(1)	0.003(1)	-0.504(1)	6.0(4)*

Table 1 *(Continued)*

Atom	*x/a*	y/b	z/c	Beq(Å^2)
C(46)	0.353(1)	0.0172(9)	−0.4491(9)	4.6(4)*
C(47)	0.2533(9)	0.0291(9)	−0.3314(9)	4.1(3)*
C(48)	0.1773(9)	0.0097(9)	−0.3052(9)	4.2(3)*
C(49)	0.106(1)	−0.073(1)	−0.375(1)	5.5(4)*
C(50)	0.008(1)	−0.128(1)	−0.386(1)	7.6(6)*
C(51)	0.182(1)	0.0686(9)	−0.2275(9)	4.7(4)*
C(52)	0.091(1)	0.053(1)	−0.214(1)	6.2(5)*
C(53)	0.103(1)	0.108(1)	−0.122(1)	5.9(4)*
C(54)	0.125(1)	0.065(1)	−0.071(1)	6.1(5)*
C(55)	0.130(1)	0.111(1)	0.021(1)	5.0(4)*
C(61)	0.180(1)	0.0738(9)	0.2763(9)	4.6(4)*
C(62)	0.177(1)	0.000(1)	0.290(1)	6.8(5)*
C(63)	0.196(1)	0.014(1)	0.375(1)	8.0(6)*
C(64)	0.219(1)	0.093(1)	0.441(1)	6.6(5)*
C(65)	0.220(1)	0.164(1)	0.424(1)	6.3(5)*
C(66)	0.200(1)	0.153(1)	0.341(1)	5.9(4)*
C(67)	0.1522(9)	0.1161(9)	0.1607(9)	4.0(3)*
C(68)	0.1394(9)	0.0742(9)	0.0751(9)	3.8(3)*
C(69)	0.143(1)	−0.0085(9)	0.0635(9)	4.5(4)*
C(70)	0.136(1)	−0.082(1)	−0.016(1)	6.1(5)*
C(71)	0.7255(8)	0.3734(8)	0.0918(8)	3.3(3)*
C(72)	0.812(1)	0.442(1)	0.144(1)	5.2(4)*
C(73)	0.886(1)	0.422(1)	0.151(1)	6.4(5)*
C(74)	0.869(1)	0.332(1)	0.106(1)	5.7(4)*
C(75)	0.781(1)	0.2651(9)	0.056(1)	4.8(4)*
C(76)	0.7089(9)	0.2853(9)	0.0493(9)	4.2(3)*
C(77)	0.5766(8)	0.3547(8)	0.0178(8)	3.2(3)*
C(78)	0.5273(8)	0.4031(8)	0.0444(8)	2.9(3)*
C(79)	0.5824(8)	0.4677(8)	0.1269(8)	3.2(3)*
C(80)	0.570(1)	0.541(1)	0.191(1)	5.0(4)*
C(81)	0.4395(8)	0.3790(8)	−0.0047(8)	3.0(3)*
C(82)	0.3905(9)	0.4317(8)	0.0324(9)	3.8(3)*
C(83)	0.2950(9)	0.3979(8)	−0.0274(8)	3.7(3)*
C(84)	0.258(1)	0.4633(9)	0.0160(9)	4.4(4)*
C(85)	0.2392(9)	0.4551(8)	0.0914(8)	3.5(3)*
C(91)	0.1360(9)	0.5978(9)	0.3085(9)	4.1(3)*
C(92)	0.076(1)	0.6327(9)	0.302(1)	4.8(4)*
C(93)	0.042(1)	0.651(1)	0.369(1)	5.9(4)*
C(94)	0.068(1)	0.634(1)	0.433(1)	6.2(5)*
C(95)	0.127(1)	0.598(1)	0.440(1)	6.4(5)*
C(96)	0.164(1)	0.5812(9)	0.374(1)	4.9(4)*
C(97)	0.1892(9)	0.5096(8)	0.2094(8)	3.5(3)*
C(98)	0.2172(8)	0.5184(8)	0.1446(8)	3.3(3)*
C(99)	0.2129(8)	0.5968(8)	0.1433(8)	3.4(3)*
C(100)	0.234(1)	0.6375(9)	0.0860(9)	4.3(3)*
O(110)	0.525(6)	0.3064(6)	0.0717(6)	4.7(3)
C(111)	0.017(1)	0.2662(9)	−0.005(1)	5.0(4)*
N(112)	−0.0096(9)	0.3012(9)	−0.0518(8)	5.7(4)
C(113)	0.000(1)	0.393(1)	−0.017(1)	6.9(5)*
C(114)	−0.056(2)	0.247(1)	−0.144(1)	9.8(7)*
O(120)	0.0428(6)	0.2764(6)	0.2142(6)	4.8(3)
C(121)	0.017(1)	0.325(1)	0.258(1)	5.3(4)*
N(122)	−0.0588(8)	0.2942(9)	0.2739(8)	5.7(4)
C(123)	−0.122(1)	0.196(1)	0.231(1)	8.8(6)*
C(124)	−0.091(1)	0.354(1)	0.321(1)	7.5(5)*
O(130)	0.5240(6)	0.1461(6)	−0.1995(6)	4.5(3)
C(131)	0.508(1)	0.0682(9)	−0.2485(9)	4.5(4)*
N(132)	0.5755(8)	0.0502(7)	−0.2569(8)	4.6(4)

Table 1 — *Continued*

Atom	x/a	y/b	z/c	Beq(Å^2)
C(133)	0.671(1)	0.115(1)	-0.212(1)	6.3(5)*
C(134)	0.552(1)	-0.047(1)	-0.313(1)	6.8(5)*
O(140)	0.4581(6)	0.2732(5)	-0.2258(6)	4.7(3)
C(141)	0.522(1)	0.291(1)	-0.250(1)	5.7(4)*
N(142)	0.5145(9)	0.2999(9)	-0.3203(7)	6.0(4)
C(143)	0.594(2)	0.315(1)	-0.348(2)	9.6(7)*
C(144)	0.433(1)	0.287(1)	-0.375(1)	7.3(5)*
O(150)	0.091(1)	0.308(1)	0.775(1)	18.5(6)
C(151)	0.152(2)	0.293(1)	0.746(1)	14.8(7)*
N(152)	0.116(1)	0.210(1)	0.672(1)	11.3(6)
C(153)	0.024(2)	0.165(1)	0.643(2)	15.4(7)*
C(154)	0.195(2)	0.214(2)	0.652(2)	15.9(8)*

* Starred atoms were refined isotropically, Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as: $(4/3)*[a^2*\beta(1,1) + b^2*\beta(2,2) + c^2*\beta(3,3) + ab(\cos\gamma)*\beta(1,2) + ac(\cos\beta)*\beta(1,3) + bc(\cos\alpha)*\beta(2,3)]$.

in Tables 2 and 3, respectively.

In the complex $Tb_2L_3 \cdot 5DMF$, L is a tetradentate ligand. Each L acts as bridging ligand and bonds two terbium(III) ions. The O(1) and O(2), O(5) and O(6), O(9) and O(10) atoms (from three L's) bond to Tb(2). The other six oxygen atoms of three L's bonded to Tb(1) are O(3) and O(4), O(7) and O(8), O(11) and O(12). The seventh and eighth coordinated atoms for each terbium come from the carbonyl oxygen atom of two coordinated DMF molecules. The Tb-O distances range from 2.303(4) to 2.429(4)Å (mean 2.351Å) for Tb(1)-O and 2,293(4) to 2.481(4)Å (mean 2.365Å) for Tb(2)-O. The longest is Tb(1)-O(110) (DMF) and Tb(2)-O(130) (DMF).

The coordination number of each terbium is eight. All eight donor atoms around each terbium(III) ion make up a distorted square antiprismatic coordination polyhedron. The O(7), O(8), O(110) and O(120) atoms like approximately in a

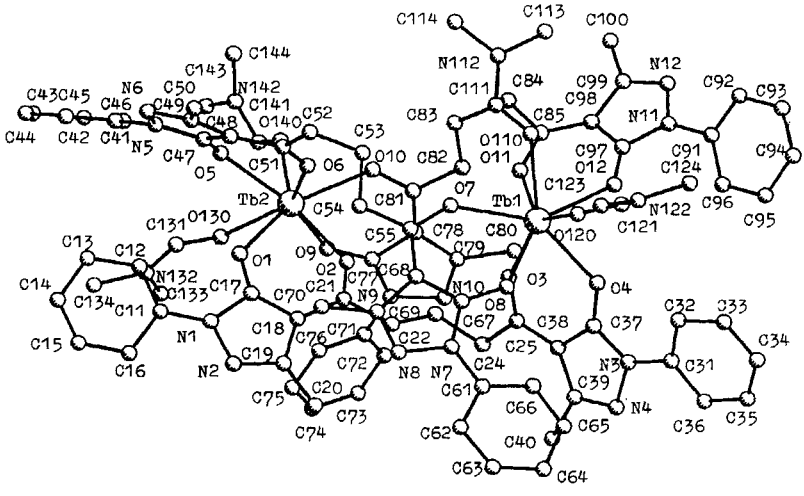

Figure 1 The molecular structure of $Tb_2L_3 \cdot 5DMF$.

Table 2 Selected bond distances (Å)*.

Tb(1)-O(3)	2.338(4)	Tb(1)-O(11)	2.380(4)
Tb(1)-O(4)	2.303(4)	Tb(1)-O(12)	2.308(4)
Tb(1)-O(7)	2.358(4)	Tb(1)-O(110)	2.429(4)
Tb(1)-O(8)	2.328(4)	Tb(1)-O(120)	2.366(4)
Tb(2)-O(1)	2.293(4)	Tb(2)-O(9)	2.284(5)
Tb(2)-O(2)	2.412(4)	Tb(2)-O(10)	2.365(4)
Tb(2)-O(5)	2.299(4)	Tb(2)-O(130)	2.481(4)
Tb(2)-O(6)	2.363(5)	Tb(2)-O(140)	2.423(4)
O(1)-C(17)	1.269(7)	C(17)-C(18)	1.411(9)
O(2)-C(21)	1.216(7)	C(18)-C(21)	1.399(9)
O(3)-C(25)	1.253(7)	C(25)-C(38)	1.433(8)
O(4)-C(37)	1.256(7)	C(37)-C(38)	1.414(8)
C(21)-C(22)	1.541(9)	C(24)-C(25)	1.540(9)
O(5)-C(47)	1.274(7)	C(47)-C(48)	1.431(9)
O(6)-C(51)	1.239(8)	C(48)-C(51)	1.405(9)
O(7)-C(55)	1.270(8)	C(55)-C(68)	1.40(1)
O(8)-C(67)	1.263(7)	C(67)-C(68)	1.409(9)
C(51)-C(52)	1.57(2)	C(54)-C(55)	1.56(2)
O(9)-C(77)	1.275(7)	C(77)-C(78)	1.438(8)
O(10)-C(81)	1.265(7)	C(78)-C(81)	1.400(9)
O(11)-C(85)	1.253(7)	C(85)-C(98)	1.430(8)
O(12)-C(97)	1.251(7)	C(97)-C(98)	1.396(8)
C(81)-C(82)	1.540(8)	C(84)-C(85)	1.518(9)
O(110)-C(111)	1.226(9)	N(112)-C(113)	1.47(1)
C(111)-N(112)	1.324(9)	N(112)-C(114)	1.48(1)
O(120)-C(121)	1.236(8)	N(122)-C(123)	1.48(2)
C(121)-N(122)	1.33(2)	N(122)-C(124)	1.47(2)
O(150)-C(151)	1.32(1)	N(152)-C(153)	1.36(1)
C(151)-N(152)	1.43(1)	N(152)-C(154)	1.44(1)

* Numbers in parentheses are estimated standard deviations.

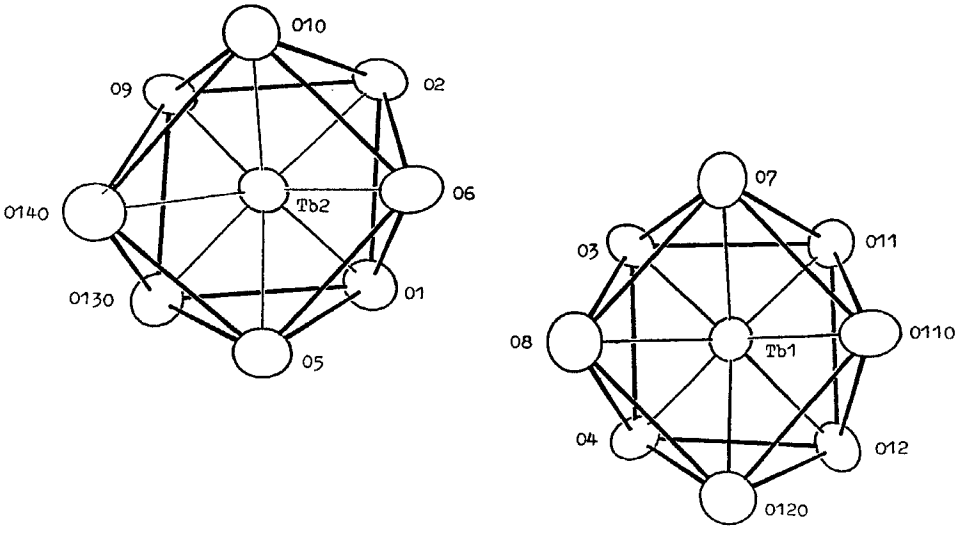

Figure 2 Coordination geometries of the terbium(III) ions.

Table 3 Selected bond angles (°).

O(3)-Tb(1)-O(4)	73.7(1)	O(7)-Tb(1)-O(11)	80.3(2)
O(3)-Tb(1)-O(7)	83.9(2)	O(7)-Tb(1)-O(12)	144.3(1)
O(3)-Tb(1)-O(8)	78.3(2)	O(7)-Tb(1)-O(110)	73.4(2)
O(3)-Tb(1)-O(11)	74.5(1)	O(7)-Tb(1)-O(120)	107.0(2)
O(3)-Tb(1)-O(12)	111.6(1)	O(8)-Tb(1)-O(11)	143.4(1)
O(3)-Tb(1)-O(110)	141.1(1)	O(8)-Tb(1)-O(12)	140.1(1)
O(3)-Tb(1)-O(120)	144.9(1)	O(8)-Tb(1)-O(110)	122.1(2)
O(4)-Tb(1)-O(7)	143.9(1)	O(8)-Tb(1)-O(120)	73.5(2)
O(4)-Tb(1)-O(8)	75.2(1)	O(11)-Tb(1)-O(12)	73.8(1)
O(4)-Tb(1)-O(11)	118.5(2)	O(11)-Tb(1)-O(110)	71.0(2)
O(4)-Tb(1)-O(12)	71.4(1)	O(11)-Tb(1)-O(120)	139.5(1)
O(4)-Tb(1)-O(110)	139.9(1)	O(12)-Tb(1)-O(110)	75.2(2)
O(4)-Tb(1)-O(120)	79.3(2)	O(12)-Tb(1)-O(120)	79.4(1)
O((7)-Tb(1)-O(8)	72.9(1)	O(110)-Tb(1)-O(120)	73.2(2)
O(1)-Tb(2)-O(2)	73.3(1)	O(5)-Tb(2)-O(9)	142.8(1)
O(1)-Tb(2)-O(5)	76.0(2)	O(5)-Tb(2)-O(10)	121.9(1)
O(1)-Tb(2)-O(6)	80.8(2)	O(5)-Tb(2)-O(130)	76.5(1)
O(1)-Tb(2)-O(9)	110.9(2)	O(5)-Tb(1)-O(140)	71.4(1)
O(1)-Tb(2)-O(10)	143.0(1)	O(6)-Tb(2)-O(9)	143.7(1)
O(1)-Tb(2)-O(130)	73.2(1)	O(6)-Tb(2)-O(10)	75.9(1)
O(1)-Sm(2)-O(140)	139.0(1)	O(6)-Tb(2)-O(130)	143.5(1)
O(2)-Tb(2)-O(5)	139.3(1)	O(6)-Tb(2)-O(140)	111.5(2)
O(2)-Tb(2)-O(6)	76.6(2)	O(9)-Tb(2)-O(10)	75.4(1)
O(2)-Tb(2)-O(9)	74.5(1)	O(9)-Tb(2)-O(130)	71.2(3)
O(2)-Tb(2)-O(10)	73.7(1)	O(9)-Tb(2)-O(140)	82.7(1)
O(2)-Tb(2)-O(130)	118.2(2)	O(10)-Tb(2)-O(130)	138.8(1)
O(2)-Tb(2)-O(140)	146.5(1)	O(10)-Tb(2)-O(140)	77.0(1)
O(5)-Tb(2)-O(6)	72.5(1)	O(130)-Tb(2)-O(140)	75.4(1)
Tb(1)-O(110)-C(111)	134.5(5)	C(111)-N(112)-C(114)	113(1)
O(110)-C(111)-N(112)	123.8(7)	C(113)-N(112)-C(114)	115.2(7)
C(111)-N(112)-C(113)	123.5(7)		
Tb(1)-O(120)-C(121)	131.6(5)	C(121)-N(122)-C(124)	122.3(7)
O(120)-C(121)-N(122)	124.3(7)	C(123)-N(122)-C(124)	117.4(7)
C(121)-N(122)-C(123)	119.5(7)		
O(150)-C(151)-N(152)	115(2)	C(151)-N(152)-C(154)	103.1(9)
C(151)-N(152)-C(153)	112(1)	C(153)-N(152)-C(154)	145(2)

Table 4 Dihedral angles between planes identified in the complex.*

Plane No.	Plane No.	Dihedral angle (°)
1	2	2.3
1	3	74.8
1	4	75.0
2	3	76.6
2	4	76.7
3	4	2.1

* No. 1: O(7), O(110) and O(120); No. 2: O(3), O(4), O(11) and O(12); No. 3: O(5), O(6), O(10) and O(140); No. 4: O(1), O(2), O(9) and O(130).

plane (Plane 1). The O(3), O(4), O(11) and O(12) atoms make up Plane 2 (Fig. 2). The distances between Tb(1) and the two planes are −1.2787Å and 1.2507Å, respectively. Plane 3 consists of O(5), O(6), O(10) and O(140) atoms, and Plane 4 of O(1), O(2), O(9) and O(130) atoms (Fig. 2). The distances between Tb(2) and the two planes are −1.2369Å and 1.2769Å, respectively. The dihedral angles between the planes are listed in Table 4. The two coordination polyhedra show little difference.

There are some changes in bond distances and angles when DMF coordinates to terbium ions (Table 2 and 3). Resonance forms of DMF should be $O{=}CH\text{-}N(CH_3)_2 \leftrightarrow {}^{-}O{=}CH = N^{+}(CH_3)_2$. Though this should give a short C-N distance, the distance found in the crystal is long. The coordinated DMF molecules are similar in structure.

All the β-diketones in the complex coordinate to terbium ions in enol forms with a negative charge (the hydrogen of OH is displaced by terbium). From the C-O distances we conclude that the negative charge is delocalized in the three β-diketone units coordinated to Tb(1). The charges of the other three β-diketones bonded to Tb(2) are partially delocalized and the oxygen atom connected to the pyrazoline ring has a negative charge. The title complexes have very strong green fluorescence with maximum emission around 545 nm ($^5D_4 \rightarrow {}^7F_5$).

Supplementary Material

Full lists of anisotropic temperature factors, bond distances and angles, and calculated and observed structure factors are available on request from the authors.

References

1. X. Dong, F. Liu and Y. Zhao, *Huaxue Xuebao,* **41**, 848 (1983).
2. L. Yang, R. Yang, W. Dong and J. Liu, *Huaxue Xuebao*, **47**, 633 (1989).
3. L. Yang and R. Yang, *Huaxue Xuebao,* **47**, 911 (1989).
4. L. Yang and R. Yang, *Gaodeng Xuexiao Huaxue Xuebao,* **10**, 225 (1989).
5. L. Yang *et al.*, unpublished data.
6. L. Yang and R. Yang, *Lanzhou Daxue Xuebao,* **24**, 134 (1988).