

Tetrahedral Complexes of Europium with [Gd-Tr-P-G-L-M], NK-2 Triangular Antiprismatic

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Complexes of europium(III) with the ligands [Gd-Tr-P-G-L-M], NK-2, and triangular antiprismatic ligands were synthesized and characterized. The complexes were studied by X-ray diffraction, IR, UV-Vis, and EPR spectroscopy. The structures of the complexes were determined by X-ray diffraction. The complexes were found to be stable in aqueous solution. The complexes were also studied by EPR spectroscopy. The complexes were found to be stable in aqueous solution. The complexes were also studied by EPR spectroscopy. The complexes were found to be stable in aqueous solution.

Keywords: -2, i, R, Bi

1988 *et al.* 1,2, 16 i d i fi il ii
C- i B . l6 il l6 d l6 l6i l6 l6 ii
i ii -2 l6 ii . l6 d - -
l6 - - i l6 B i i -2 .
1993/1994 l6 l6 d i d Sd B l6 B B -
i S¹ R l6i il i D d₆ 3,4 d i D d₆ d
D d₆ / 2 5 . A l6 B d d l6 l6 i d R d i d i -
d, l6 d l6 d i S B d, l6 il i i i B i B -
i . B *et al.* 3 d i l6 *et al.* 4 d l6 i B i B i
i B i , l6i l6 il i d (R i l6
4) d B i B B l6 i i l6 il il6
l6 l6 B i B i B . A d *et al.* 5 i d d i i l6 -
d i B B d d d d i i d i i B -
i , i d d B i i i i . l6 i -

d d b b i 3.5 Å d - i b. i l6i l6 l6
 b d l6 i , l6i l6 l6 d i i b 5 .
 l6 l6 i b b i l6 d i d -
 tl b i b d b d b il6 6 8 , l6i l6 i l6 d
 d i d l6 i d i i , b i l6
 i d b i bi- i b i b i l6 tl
 did. l6 i , l6 l6 i b l6 b l6 tl
 -2 i d, l6 l6 i ii d l6 ³ α
 i i b b l6 b i b b d. i b ,
 l6 d d l6 i b b b d b i d i l6
 l6 l6 i b d i b b . l6 i b b
 b i d l6 i b b d i i b i l6 . i -
 i l6i l6i i b i b d i l6 b tl .
 l6 b i d i b d il6 l6 i b b l6 d .

B A

P t l s t s s: tl l6 i d l6 l6 l6 l6 d i l6 i d
 i tl l6 i A b d Bi 430A.D i b l6 l6 d b d b l6 d
 i b 9 . C b i l6 b d d i b -1- b - i -
 b i - l6 l6 i l6 b l6 l6 (B) i d i l6 b tl . C b i
 d b i b b (i b C₈, 4.6 × 250 , 5 μ).
 NMR ¹³C r m s: l6 tl i 3 . l6 b i -
 d i i 500 b , i 500 . A b
 d d 295 l6 i i l6 l6 i b l6i , l6i l6 -
 d l6 tl l6 l6 l6 295 318 . l6 S i S i
 l6 S i l6 i b l6i b l6 d l6 S 2D , C S i ,
 b , l6 l6 i i i b d : 150 d 300 , 200 d 250 S i b 70
 C . Add i b A i C b i b C i C (AC - -C)
 30 d d . A b d d i l6 b 4.3 (i ,
 A).
 V z w s t s: l6 ³ α b d l6 AC - -C
 T m r r l c o t c m e s t s o t N H o b s: l6 b Δδ/Δ b
 b d l6 1D d d 295 , 303 , 308 , 313 d 318 . S i (300)
 T NOE s: l6 - tl did i d l6
 S t r e t o : l6 l6 l6 i b l6 tl i d
 l6 b i b d i C b l6 d (D C) 11 . C i b b d
 i l6 C /3 (i i b C i b tl) i b 12 , l6i l6 -
 i tl b . A d i l6 b l6 tl d i d
 trans. l6 l6i b S b α C i d . l6 i b i b d l6 d i i i , l6i l6
 b b d i l6 b - b i l6 d i b et al. 13 il6 i i b . Ad i-
 b i ε=2 d i l6 b b i , d i l6 d i l6 l6 l6
 C /3 i b 12 . l6 i D C i b i 1000 , l6i l6 -
 d d b 20 30%. l6 d l6 C A b b
 i b b i 14,15 . i b , 2500 - i i i d i i
 i d . l6 i d S i b d (i l6 i i - i i b il6 16).
 l6 d i i (b D) l6 i b i i

$\bar{V}_i = V_0 \sum_{j=1}^{NC} x_j v_{ji} \quad i = 1, 2, \dots, NP;$
 $\bar{J}_i = \sum_{j=1}^{NC} x_j J_{ji} \quad i = 1, 2, \dots, NQ;$
 with $\sum_{i=1}^{NC} x_i = 1$

16 di i , d - 6 0.1 Å d 16 i-
 6 . i 6, S 16 it did 807 i6 i d. l6i - 16 16 16
 i 6 Ddi 16 i6 . l6 i -
 16 6 i l6 d 16 basis set, i d l6 6 - i 16
 i6 . Add i i 6, 6 i 6 l6 d, i il6 i 10 6 6
 16 6 d i 6 6 di d d.
 C to o s t s t c k s o w o r m t o s t t o r t c t o r m t NMR
 t : 16 , l6 i i i d l6 ³ α i i 6 6 16 6 -
 i i 16 i6 i6 i d 6 6 d. l6 i i 16 6 -
 d 6 i 16 16 6 6 l6 d i 6 i 17 6 i 16 6 A
 18, 19 . l6 i i 6³ α 6 6 - i 6 6 d 16 -
 i i 6 6 - 6 6 i l6 i 20 . B d 16 d d l6 i 6 6 6 d
 6 , l6 i i 6 i l6 16 i i d i l6
 16 16 i 6 d i 6 6 , i 16 6 i l6 d 6 d i 6 6 8 . l6 16 -
 i 6 6 d i d i :

$\bar{V}_i = V_0 \sum_{j=1}^{NC} x_j v_{ji} \quad i = 1, 2, \dots, NP;$
 $\bar{J}_i = \sum_{j=1}^{NC} x_j J_{ji} \quad i = 1, 2, \dots, NQ;$
 with $\sum_{i=1}^{NC} x_i = 1$

16 \bar{V}_i 16 6 6 d i i il6 i 6 v_{ji} 16 i i il6 i 6 6 6 d
 j l6 i , V₀ i 6 , \bar{J}_i i l6 il6 6 6 d 6 6 , J_{ji} i l6
 il6 6 6 6 d j l6 i , NP i l6 i 6 , NQ i l6
 16 6 , d NC i l6 i , d x_i, i = 1, 2, ..., C 16 i i 6
 i l6 16 i i i . - 6 d l6 i i
 it di i i l6 i i i l6 . d i6 16 6 i - i i 6 il6 d d -
 i6 d i i i i 7 .



16 i S 16 S 16 S i 6 l6 i 16 it d i l6 -
 d i C , d R . l6 l6 i 6 l6 i d
 $\Delta S / \Delta$ 6 6 6 d 16 it 16 it did i d
 i 6 1. 16 d i d il6 3 5 . 16 i-
 i 16 16 8 d 10 16 i 3 d 4 , 16 i
 5 l6 i 6 i 16 d. l6 S i d d l6 6
 i i 6 6 16 i i . 1. d 6
 16 16 6 6 6 l6 i t , 16 il6 6 6 i-
 i (6 1) i i d i i .
 l6 i d i 16 d l6 i 6 d i i l6 it i i
 6 i i 6 i 6 i . l6 6 i 6 i i 3 5 .
 16 , l6 i l6 i i i l6 6 i 16 it d -
 i d i 6 d l6 i 6 6 6 i d d i d .

R	C6 i b l6i				l6	Δδ/Δ /
	α-C	β-C	γ-C	δ-C		
6	7.77	3.91	1.78	1.95	ε- ₂ () 6.82; () 7.16	0.96
7	7.95	4.20	3.02		(1) 10.81; 2 7.02; 7 7.30	2.62
8	8.13	4.21	3.02; 2.99	2,6	7.02 3,5 7.12; 4 7.46	3.10
9	8.24	3.59				3.10
10	8.33	4.11	1.52	1.49	0.88; 0.79	3.65
11	8.11	4.11	2.00; 1.98	2.45; 2.39		3.30

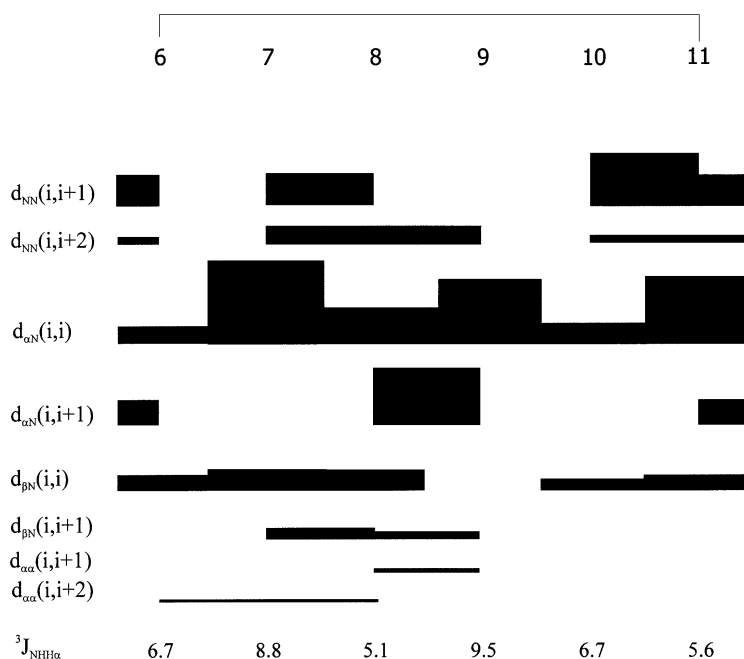
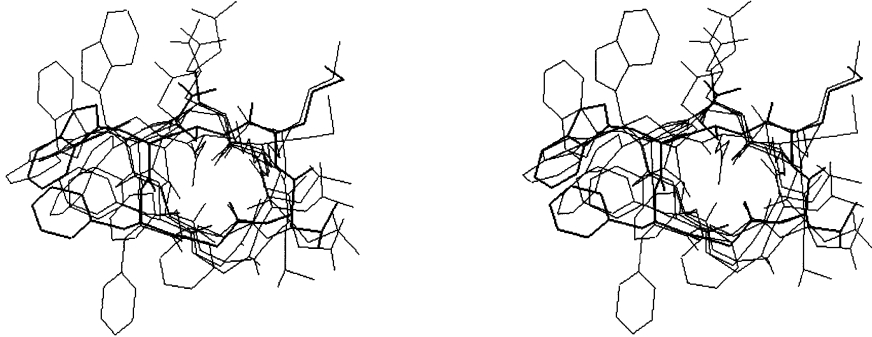


Fig. 1. ¹³C NMR chemical shifts (δ) and coupling constants (J) for the molecule. The diagram shows the positions of the carbon atoms (6-11) and the corresponding coupling constants. The values of ³J_{NHHa} are given in the table below.

³ J _{NHHa}	6.7	8.8	5.1	9.5	6.7	5.6
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A



B

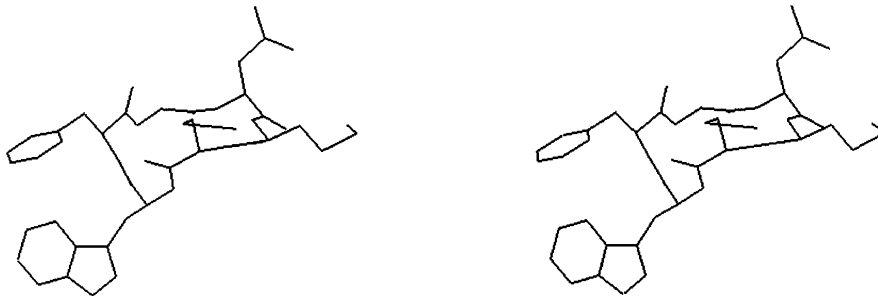


Fig. 2. S_{ij} i l6 ii i il6 ii B il6 l6l6 l6 3% -
 B -2 i (A), d l6 B d i (B).

il l6 i 10 l6 i B B l6 i i il
 d -2 l6 i i . B d i 5 l6 l6 i i -
 i i B i B i B i i . l6 il d l6 l6 i d
 β - B l6 ii l6 il l6 i 7 d l6 8 d
 i iB l6 d i d - d B d B -
 i i B -2 i 1027 B (¹-A ²- ³- l6 ⁴-D ⁵-
⁶) B (2 β -5 β) 22 . l6, il d B i , d
 β - d il6 ³- l6 ⁴ d ⁶- ¹i i+1 d i+2, i B 23 .
 B B Bd i iB ii l6 B l6 d i B il
 did l6 3,5 . l6 B i β - i -
 i B d i 5 d 'i l6 : - -B- d
 B - l6 -B . d ' β - B d i l6 B i 3 ,
 i il d l6 l6 i B l6 i ii l6
 il did . B l6 B d l6 B γ - .
 B l6 d 7 d i i .

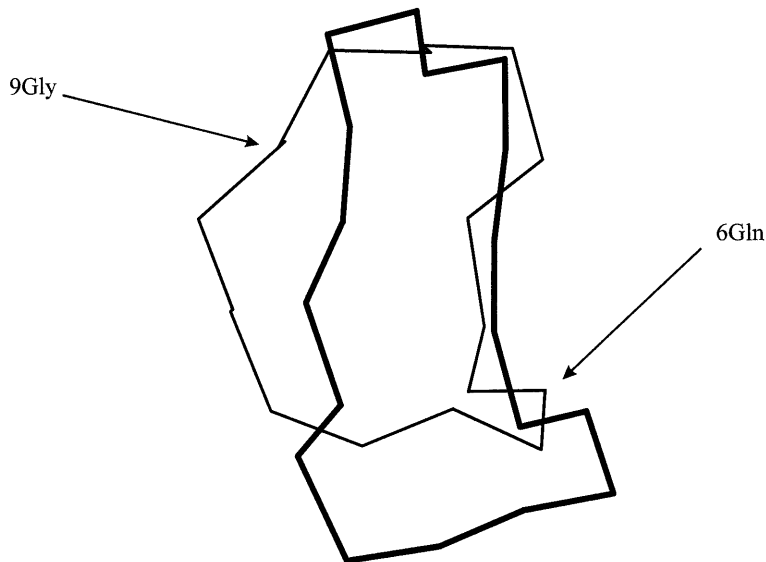


Fig. 3. S_1
 i il6 l6 l6 l6 i i b il6 i di l6i d . l6i b : i S₁ -
 i d il6 d . 4 . l6 9 6 i i l6 b . S₁ D
 = 0.42 Å.

C C S_1 S_1
 l6 i b -2 i b i i d b
 il6 il6 l6 b b d i b i b i b l6, l6 i di -
 d i , b b i d i l6 d l6 l6 d
 d i dl6 . b l6 i b d b d l6i l6d i i -
 b i , b l6 l6 d d l6 d i d l6 b l6 i i b
 il6 i b d,d i l6 i b i b i l6
 il did . l6i i i i l6 i b b i
 b i b il di i il d l6 l6 i b i b d .

A b d
 l6i d l6 i i S₁ d n (D /8290-4-0129-1). l6 b b -
 i id i l6 A d i C C (A S₁) i d n , b d, d di i b
 C l6 S₁ b d b (C) i , b d . S₁ i i i b l6i l6
 d i b l6 i .

R R C S

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