

## Dimeric hexakis(4-methylbenzoato)-bis(1,10-phenanthroline)dysprosium(III)

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Received 21 October 2004

Accepted 9 December 2004

Online 15 January 2005

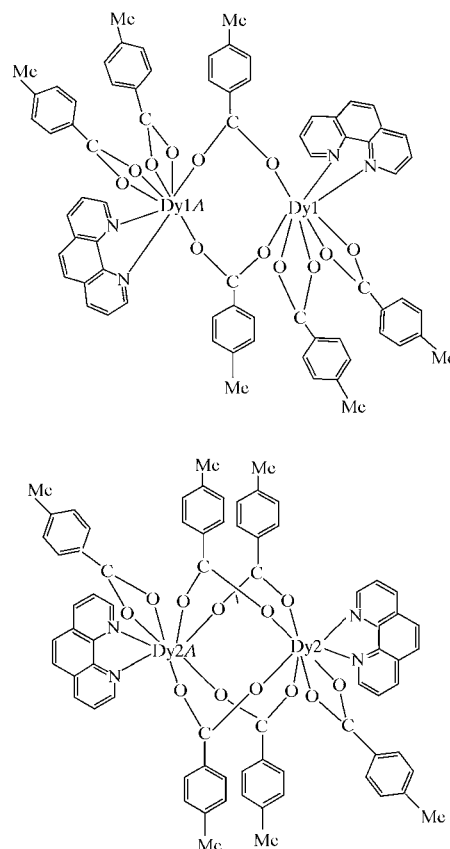
The title compound,  $[\text{Dy}_2(\text{C}_8\text{H}_7\text{O}_2)_6(\text{C}_{12}\text{H}_8\text{N}_2)_2]$ , forms binuclear complexes, *viz.* di- $\mu$ -4-methylbenzoato- $\kappa^4 O:O'$ -bis[bis-(4-methylbenzoato- $\kappa^2 O, O'$ )(1,10-phenanthroline- $\kappa^2 N, N'$ )-dysprosium(III)] tetra- $\mu$ -4-methylbenzoato- $\kappa^8 O:O'$ -bis[(4-methylbenzoato- $\kappa^2 O, O'$ )(1,10-phenanthroline- $\kappa^2 N, N'$ )dysprosium(III)]. There are two independent binuclear complexes in the asymmetric unit, both of which are centrosymmetric. In one, the  $\text{Dy}^{\text{III}}$  ions are linked by two bridging 4-methylbenzoate groups, while in the other, the  $\text{Dy}^{\text{III}}$  ions are linked by four bridging 4-methylbenzoate groups. The remaining 4-methylbenzoate groups and 1,10-phenanthroline units coordinate to just one metal ion in bidentate modes.

### Comment

Lanthanide carboxylate complexes containing 1,10-phenanthroline (phen) or 2,2'-bipyridine (2,2'-bipy) have been widely studied. Complexes of this type display a variety of structural types, with high stability and intense fluorescence. We have synthesized the novel title complex,  $[\text{Dy}(4\text{-CH}_3\text{C}_6\text{H}_4\text{COO})_3(\text{phen})_2]$ , (I), using 4-methylbenzoic acid and 1,10-phenanthroline (phen) as ligands with dysprosium(III) *via* a conventional solution reaction method. Two kinds of constitution exist in the complex. We report here the crystal structure of (I).

The structure of (I) contains two independent centrosymmetric dimers (Fig. 1), unlike lanthanide complexes of 4-methylbenzoic acid, such as the one-dimensional polymer  $\text{Eu}(4\text{-CH}_3\text{C}_6\text{H}_4\text{COO})_3$  (Jin *et al.*, 2001), but similar to the binuclear complex  $\text{Sm}_2(\text{C}_8\text{H}_7\text{O}_2)_6(\text{C}_{10}\text{H}_8\text{N}_2)_2$  ( $\text{C}_{10}\text{H}_8\text{N}_2$  is 2,2'-bipyridine; Li & Zou, 2003).

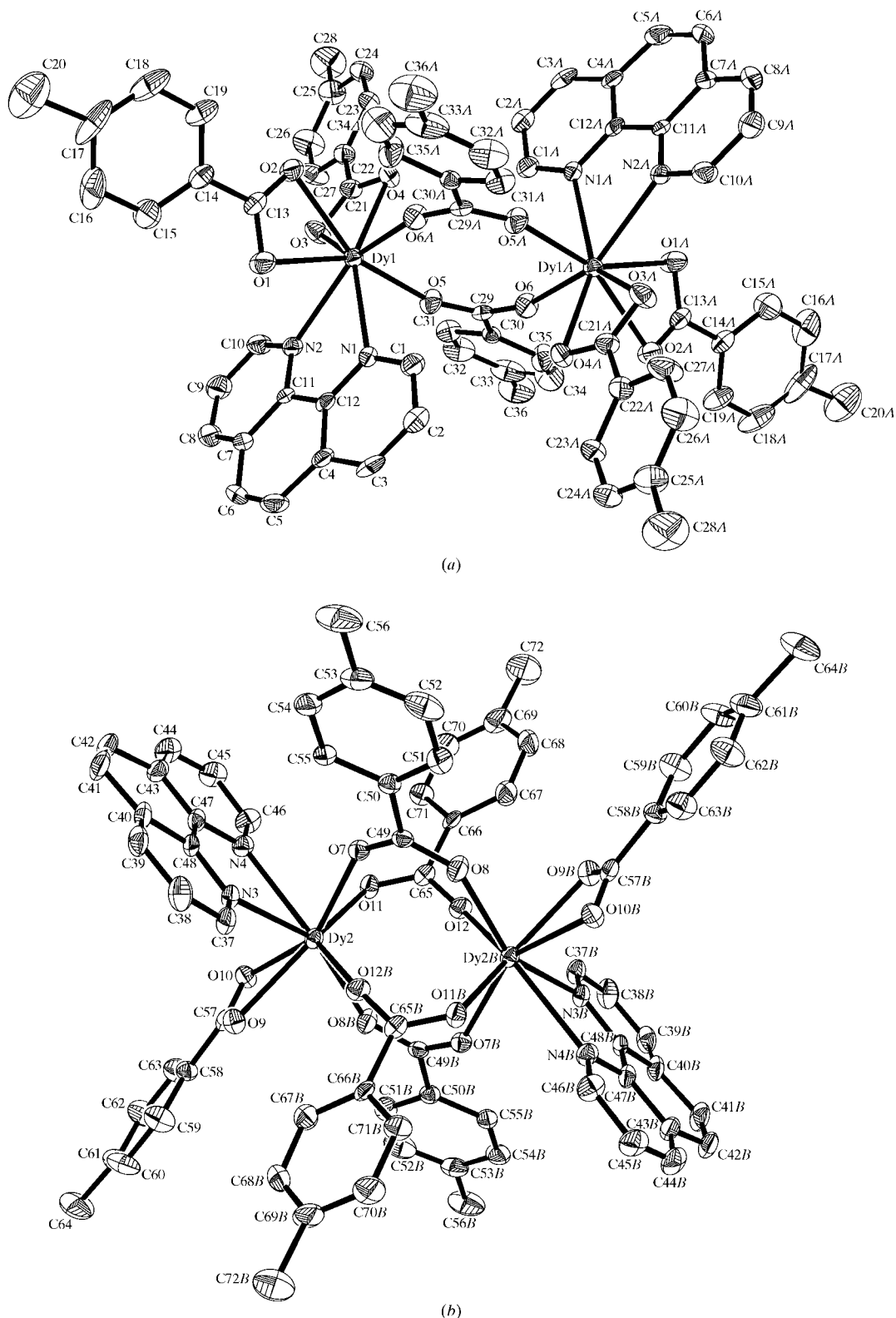
Each Dy1 ion is coordinated by two O atoms from two bridging 4-methylbenzoate groups, four O atoms from two chelating 4-methylbenzoate groups and two N atoms from one 1,10-phenanthroline (Fig. 1*a*), and each Dy2 ion is coordinated by four O atoms from four bridging 4-methylbenzoate groups, two O atoms from one chelating 4-methylbenzoate group and two N atoms from one 1,10-phenanthroline (Fig. 1*b*). The coordination number of each type of Dy ion is eight, but their coordination environments are different; the coordinated polyhedron of Dy1 is an irregular dodecahedron (Fig. 2*a*), while that of Dy2 is a square antiprism (Fig. 2*b*).



The two centrosymmetric dimers of (I)

Two carboxylate groups rarely link to the same central ion in chelating coordination mode. The complex containing Dy2, however, is typical of lanthanide carboxylate complexes. For example,  $\text{Sm}_2(\text{C}_8\text{H}_7\text{O}_2)_6(\text{C}_{10}\text{H}_8\text{N}_2)_2$ ,  $[\text{Eu}(3\text{-CH}_3\text{C}_6\text{H}_4\text{COO})_3(\text{phen})]\cdot\text{H}_2\text{O}$  (Jin *et al.*, 1993) and  $\text{Eu}_2(3,4\text{-DMBA})_6(\text{phen})_2$  (3,4-DMBA is 3,4-dimethylbenzoate; Wang *et al.*, 1999) are of this type.

The Dy1–O distances in (I) range from 2.256 (5) to 2.433 (5) Å, with an average of 2.278 (5) Å, the Dy1–N distances are 2.529 (6) and 2.547 (6) Å, and the distance between the two Dy ions is 5.305 (6) Å. The Dy2–O distances range from 2.276 (5) to 2.471 (5) Å, with an average of 2.3555 Å, the Dy2–N distances are 2.576 (6) and 2.579 (6) Å, and the distance between the two Dy ions is 4.200 (6) Å.

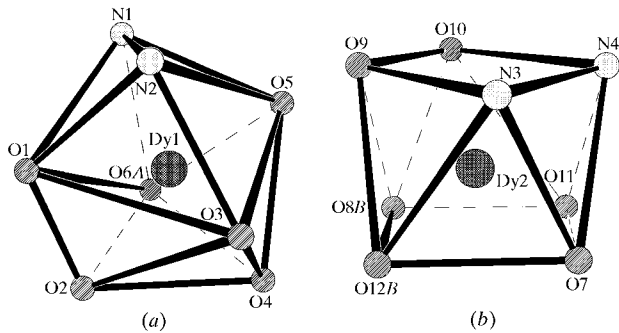


**Figure 1**

Views of the components of the title complex. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry codes: (A)  $1 - x, 1 - y, 1 - z$ ; (B)  $1 - x, 1 - y, -z$ .]

The Dy–O or Dy–N distances involving Dy1 and Dy2 differ only slightly between the two metal sites, but the Dy–Dy distances are significantly different. The Dy1···Dy1 distance is longer than Dy2···Dy2 because of the different

numbers of bridging ligands. The molecular structure and coordination environment of the title complex are quite similar to that observed for the dimer  $\text{Eu}(4\text{-CH}_3\text{C}_6\text{H}_4\text{-COO})_3(\text{phen})$  (Jin *et al.*, 1994).



**Figure 2**  
Schematic representations of the coordination geometries of the two independent Dy ions in (I) [symmetry codes: (A)  $1 - x, 1 - y, 1 - z$ ; (B)  $1 - x, 1 - y, -z$ ].

## Experimental

4-Methylbenzoic acid (1.5 mmol, 204 mg) was dissolved in ethanol (20 ml) and the pH of the solution was adjusted to 5–6 using 2 M NaOH. Ethanol solutions of 1,10-phenanthroline (0.5 mmol, 90 mg) and  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$  (0.5 mmol, 189 mg) were added successively. The mixture was heated under reflux with stirring for 2 h and then kept at ambient temperature for 6 d. Crystals of (I) were obtained and used for IR and X-ray diffraction analyses. Analysis calculated: C 57.8, N 3.7, H 3.9%; found: C 58.0, N 3.6, H 3.9%.

### Crystal data

$[\text{Dy}_2(\text{C}_8\text{H}_7\text{O}_2)_6(\text{C}_{12}\text{H}_8\text{N}_2)_2]$   
 $M_r = 1496.22$   
 Triclinic,  $P\bar{1}$   
 $a = 12.760$  (8) Å  
 $b = 13.346$  (9) Å  
 $c = 19.758$  (13) Å  
 $\alpha = 91.619$  (12)°  
 $\beta = 97.925$  (11)°  
 $\gamma = 106.440$  (10)°  
 $V = 3188$  (4) Å<sup>3</sup>

$Z = 2$   
 $D_x = 1.559$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 987 reflections  
 $\theta = 3.1$ – $23.7$ °  
 $\mu = 2.39$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prism, yellow  
 $0.22 \times 0.18 \times 0.12$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.541$ ,  $T_{\max} = 0.750$   
 16 586 measured reflections

11 165 independent reflections  
 7695 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$   
 $\theta_{\text{max}} = 25.0$ °  
 $h = -15 \rightarrow 14$   
 $k = -13 \rightarrow 15$   
 $l = -20 \rightarrow 23$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.043$   
 $wR(F^2) = 0.121$   
 $S = 1.11$   
 11 165 reflections  
 811 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.0276P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.003$   
 $\Delta\rho_{\text{max}} = 0.86 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.96 \text{ e \AA}^{-3}$

We were unable to locate all the H atoms from difference maps; methyl H atoms were particularly poorly resolved and disordered. For the final refinement, all H atoms were placed in geometrically idealized positions using *SHELXL97* HFIX 43 and 33 commands (for CH and CH<sub>3</sub> groups, respectively) and constrained to ride on their parents atoms [ $\text{C}-\text{H} = 0.93$  and  $0.96$  Å, and  $U_{\text{iso}}(\text{H}) = 1.2$  to  $1.5U_{\text{eq}}(\text{C})$ ].

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

This work was partly supported by the Scientific Research Foundation for Returned Overseas Chinese Scholars, Beijing Municipal Government, and the project was sponsored by the Scientific Research Foundation for Returned Overseas Chinese Scholars, State Education Ministry.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1354). Services for accessing these data are described at the back of the journal.

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